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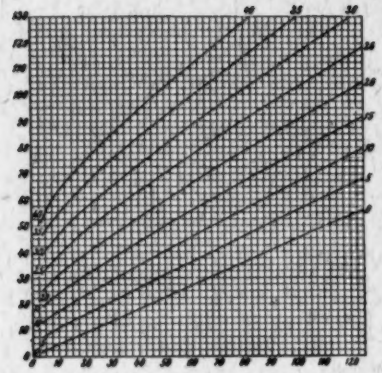

TABLES AND NOMOGRAMS OF HYDROCHEMICAL ANALYSIS

by I. Yu. Sokolov

Translated from Russian

Upon completion of analytical experiments, every research chemist, whether he uses a "test tube" or a "пробирка," must calculate his findings in the international language of figures in two forms (weights and equivalents), and often three (weights, equivalents and percent-equivalents), and then compare experimental data with theoretical values.

Technicians and statisticians working with the results of hydrochemical analyses performed at different times by different laboratories inevitably face the problem of converting their figures to one system.

All such calculations are considerably simplified by the use of the tables and nomograms in this book, originally published by the State Scientific and Technical Press for Literature on Geology and the Conservation of Mineral Resources, Moscow.

All the tables and nomograms are based on analytical results expressed in the form widely used in hydrogeological practice—milligrams per liter (weight form) and milligram-equivalents per liter (equivalent form). For calculation of percent-equivalents, the sum of cation equivalents and the sum of anion equivalents are taken as 100% each. Several new tables are presented for the first time, and the many tables for converting water-analysis results from one form to another make it possible to find the milligram-equivalents for any practically possible content of a component in water, accurate to the second decimal place, and the weight content of substances to tenths of a milligram.

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International atomic weights (Appendix)

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USE OF GAS-LIQUID CHROMATOGRAPHY FOR THE ANALYSIS OF CERTAIN HYDROCARBON MIXTURES

B. A. Rudenko, S. S. Yufit, L. N. Ivanova, and V. F. Kucherov

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In studying the dehydrogenation of branched hexenes [1,2], we were faced with the problem of analyzing catalyzates containing ethylene and diene hydrocarbons. There were particular difficulties in the development of methods for analyzing mixtures of isoprene and 2,3-dimethylbutadiene with various ethylene hydrocarbons as it is not always possible to separate such a mixture sufficiently reliably by fractional distillation, even on extremely efficient columns. Chemical methods of analyzing such mixtures are also very crude [3] and cannot be used to determine the composition of catalyzates containing mixtures of dienes. Many problems in the analysis of liquid and gaseous organic materials are now solved very successfully by gas-liquid chromatography. However, the literature contains comparatively sparse information on the use of this method in the analysis of liquid mixtures of various dienes and most work is largely concerned with the analysis of gaseous mixtures containing butadiene [4,5].

For the analysis of certain mixtures of hydrocarbons, including dienes, we constructed a simple instrument for gas-liquid chromatography, which was found to be quite efficient for substances boiling below 150°. The plan of the instrument is given in Fig. 1. As in all systems of this type, the main parts of our instrument were a chromatography column, an evaporator-injector, and a measuring cell for analysis of the gas emerging from the column.

The chromatography column 1 was a glass U-tube with an internal diameter of 6 mm, each arm of which was 1 m long. The tube was packed with kieselguhr (particle size 0.2-0.5 mm), moistened with the stationary liquid phase, for which we used silicon or vaseline oils, dibutyl phthalate, or tricresyl phosphate. To 50 g of kieselguhr was added 14-15 g (30%) of stationary liquid phase, and the normal density of the packing was 0.4-0.5 g/ml [4]. The column was fitted with an electric heater; the temperature of the column was maintained with an accuracy of about ± 0.5° during operation. The carrier gas was hydrogen supplied from tank 3. When a good reducing valve of any sort was used, it was unnecessary to use additional devices for maintaining constant pressure (buffer spaces, liquid gaps or various regulators). The hydrogen pressure was controlled with a 2.5 atm manometer 4 with a scale division of 0.02 atm. The gas consumption was measured with a flowmeter 5.

After passing through a column with a drying agent, the hydrogen entered the evaporator for the liquid analyzed 6, which also served as the injector of the mixture analyzed in our instrument. In the qualitative analysis of gases and liquids, they were introduced into the column by means of a syringe through a rubber cap which covered the upper end of the evaporator. Important factors in the quantitative analysis of liquid mixtures are the liquid evaporation rate [6] and the constancy of the volume of the sample introduced, which substantially facilitates processing of the analysis results. In quantitative analysis of mixtures, the injection should be very accurate as even 0.002 ml of liquid can give a deflection of 3.5-4 mv on the recorder. Our evaporator-injector, which is illustrated in

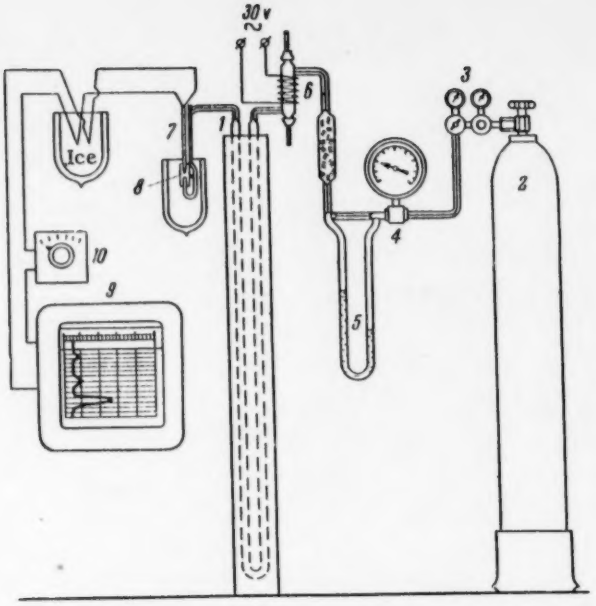

Fig. 1. Plan of instrument. 1) Chromatography column; 2) hydrogen tank; 3) reducing valve; 4) manometer; 5) flowmeter; 6) evaporator-injector; 7) burner of microflame detector; 8) thermocouple; 9) ÉPP-09 recording potentiometer; 10) source of variable dc voltage.

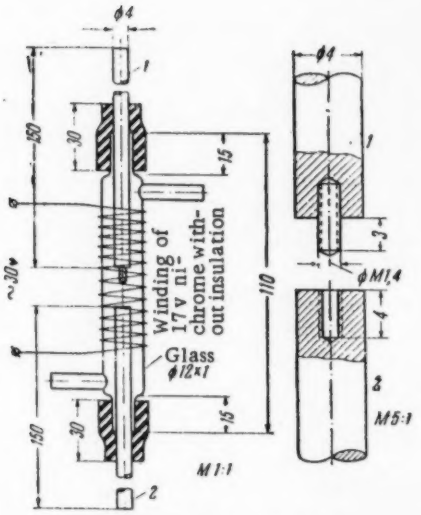

Fig. 2. Evaporator-injector.

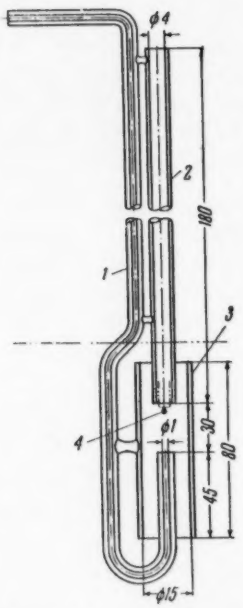

Fig. 3. Burner. 1) Gas inlet tube; 2) thermocouple tube; 3) guard tube; 4) thermocouple bulb.

Fig. 2, meets these requirements. It consists of a glass tube, with gas inlet and outlet tubes, which is fitted with a heater winding, giving a temperature of 100-120° at a voltage of 30 v, which guarantees an adequate evaporation rate. Through the ends of the tube were passed two metal rods 1 and 2, which screwed together and were held quite tightly by sections of rubber vacuum tubing, but which could be moved along the axis of the tube. The amount of liquid sample introduced was determined by the volume of the free space remaining between the pin of rod 1 and the bottom of the threaded opening of rod 2 when they were screwed together. By varying the size of this space it was possible to change the volume of sample introduced over a wide range and in our experiments this did not exceed 0.0015-0.0020 ml. The movement of the rods was such that their junction could be withdrawn, making it possible to introduce a sample of the liquid analyzed without upsetting the operation of the instrument.

When the rods were unscrewed, a sample of analysis liquid introduced in this way evaporated and its vapor was carried by a steady stream of hydrogen into the chromatography column, where the separation occurred. For analysis of the gas emerging from the column which contained the separated components of the analysis mixture, we used a method based on the measurement of the flame temperature of the gas emerging from the column. For this purpose we constructed a special microflame detector, which was considerably simplified in comparison with those described previously [7]. The detector burner was made of glass; its construction is shown in Fig. 3. As is known [7,8], the flame temperature of a gas emerging from a chromatography column and burnt in a burner depends on its composition. In our instrument this temperature was measured with a chromel-alumel thermocouple which was introduced into tube 2. The bulb of the thermocouple was set at such a height above the burner outlet that the initial thermal emf equalled 20-22 mv. To increase the sensitivity of the instrument, the ÉPP-09 recording potentiometer, which registered the thermal emf, was graduated over the range of 0-5 mv. For this purpose it was necessary to resort to partial compensation of the emf of the thermocouple by means of any source of dc voltage, for example, a PP laboratory potentiometer or IRN-250 instrument. The ÉPP-09 recorder had a scan time of 4 sec and the paper speed was 120 mm/hr. The time for the system to reach equilibrium from beginning of operations was ~ 1 hr.

Contrary to the opinion given in the literature [9] on the instability of the zero line of a microflame detector when hydrogen is used as the carrier gas, our instrument had a zero line of high stability. The use of hydrogen as the carrier gas, which did not worsen the stability of the zero, led to an increase in the sensitivity of the instrument by a factor of 1.5-2.

By using this instrument with a column packed with kieselguhr moistened with dibutyl phthalate, we were able to carry out qualitative and quantitative analyses of catalyzates containing isopentene, isoprene, unsymmetrical methylisopropylethylene, 2,3-dimethylbutadiene, and other hydrocarbons. Preliminary graduation of the instrument on authentic mixtures showed that when the volume of the sample introduced was constant the height of the peak formed (or, more accurately, its area) was proportional to the content of the given component in the mixture. As Fig. 4 shows, the sensitivity of the instrument made it possible to detect clearly the presence of 1% of isoprene in 2,3-dimethylbutadiene or 2% of 2,3-dimethylbutadiene in isoprene, and also 0.5% of tetramethylethylene in 2,3-dimethylbutane. Since this column readily separated a mixture of isoprene and 2,3-dimethylbutadiene (Fig. 5), we carried out a quantitative analysis of the catalyzate formed by the catalytic dehydrogenation of unsymmetrical methylisopropylethylene [2]. By using calibration curves obtained on authentic mixtures of isoprene and 2,3-dimethylbutadiene for quantitative determination, we showed that this catalyzate contained 14% of isoprene and 9% of 2,3-dimethylbutadiene. According to our data, the accuracy of the analysis was ± 3%. The ratio of dienes in the catalyzate established by this method (1.5 : 1) was confirmed by distillation of the catalyzate on an efficient fractionating column, while the sum of the dienes (23%) was demonstrated by condensation with maleic anhydride. The column packed with kieselguhr moistened with dibutyl phthalate, also readily separated a mixture of 2,2- and 2,3-dimethylbutanes (Fig. 6), ether with acetone, and some ketones (Fig. 7).

Mixtures of 2,2-dimethylbutane with tetramethylethylene, ether with ethyl formate and ethyl acetate, and some others could be separated successfully on this column. Mixtures containing methanol, ethanol, acetals, and orthoformic ester could not be analyzed on the column. A column with kieselguhr moistened with tricresyl phosphate could be used to separate a mixture of pentane, hexene, hexane, and benzene (Fig. 8) and also mixtures of some unsaturated hydrocarbons and benzene (Fig. 9). The same column successfully separated mixtures of benzene,

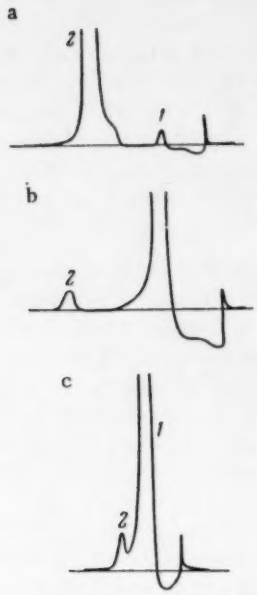

Fig. 4. Sensitivity of detector. a) 1% isoprene in 2,3-dimethylbutadiene; b) 1% 2,3-dimethylbutadiene in isoprene; c) 0.5% tetramethylethylene in 2,3-dimethylbutane.

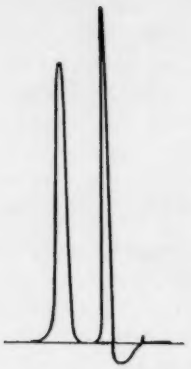

Fig. 5. Chromatogram of a mixture of 50% isoprene (peak 1) and 50% 2,3-dimethylbutadiene (peak 2).

Fig. 6. Chromatogram of a mixture of 2,2- (peak 1) and 2,3-dimethylbutanes (peak 2).

cyclohexane, cyclohexene, and cyclohexadiene, which could not be analyzed by other methods, and mixtures of 2-methyl-1,3-cyclopentadiene and 1-methyl-1-cyclopentene, boiling at 74°. It was also possible to analyze mixtures containing isoprene, piperylene, cyclopentadiene, 2,3-dimethylbutadiene, 2-methyl-1,3-cyclopentadiene, and 1,3-cyclohexadiene.

This type of analysis is extremely difficult to carry out by other methods due to the high tendency of dienes to polymerize.

We successfully used a column with kieselguhr moistened with silicone oil for the qualitative analysis of a mixture of alkenes formed by thermal decomposition of alkoxyacetylenes [10]. Analysis on such a column showed that the thermal decomposition of propoxy- and isopropoxyacetylenes formed propylene with a small amount of ethylene. Analogously it was possible to demonstrate the formation of butylene during the decomposition of n-butoxyacetylene. A mixture of isoprene and ether was separated well on the same column.

All the data presented above show that the instrument we propose makes it possible to carry out qualitative and quantitative analyses on various liquid and gaseous mixtures. Despite the simplicity of the design, this instrument has a sensitivity and accuracy which are quite satisfactory for solving many problems encountered in the work of organic chemists. In this form gas-liquid chromatography is quite suitable for the analysis of liquid mixtures containing various homologs of ethylene and butadiene and also for the analysis of some diene mixtures.

SUMMARY

Gas-liquid chromatography was applied to the analysis of mixtures of some unsaturated hydrocarbons and dienes. An instrument for gas-liquid chromatography was developed.

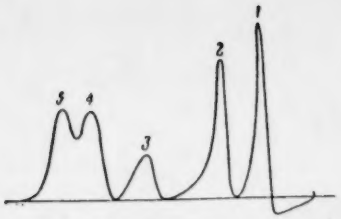

Fig. 7. Chromatogram of a mixture of aliphatic ketones: Peak 1) acetone; peak 2) methyl ethyl ketone; peak 3) methyl n-propyl ketone; 4) pinacolin; peak 5) diisopropyl ketone.

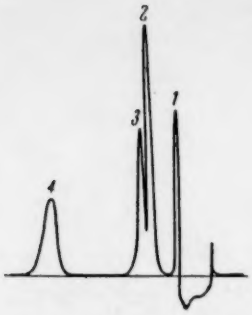

Fig. 8. Chromatogram of a mixture; 1) n-Pentane; 2) n-hexane; 3) 1-hexene; 4) benzene.

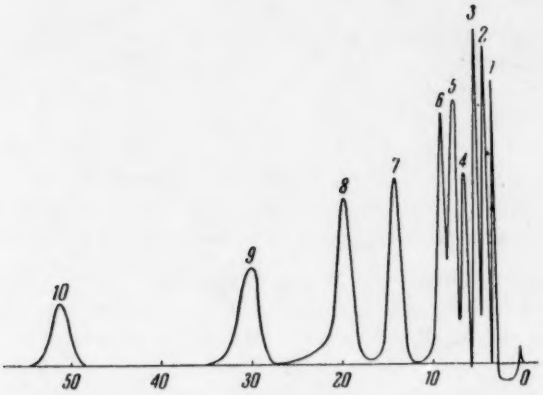

Fig. 9. Chromatogram of a hydrocarbon mixture: 1) Isopentane; 2) n-pentane; 3) 2,2-dimethylbutane; 4) 2,3-dimethylbutane; 5) 3-methylpentane; 6) n-hexane; 7) methylcyclopentane; 8) cyclohexane; 9) methylcyclohexane; 10) benzene.

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THEORY OF THE PHYSICAL ADSORPTION OF GASES AND VAPORS AND ADSORPTION PROPERTIES OF ADSORBENTS OF VARIOUS NATURES AND POROUS STRUCTURES

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In modern technology, increasing use is being made of sorption methods for the separation of gas mixtures, fine purification and drying of gases, recovery of volatile solvent vapor, purification of solutions, etc. Most of them are based on the physical adsorption of gases, vapors, and dissolved substances.

The intensification of technological sorption processes by the choice of effective adsorbents and refinement of conditions and the planning of new processes requires the creation of calculation methods based on the theory of physical adsorption. The theory of adsorption is also of definite importance in the development of methods for synthesizing adsorbents with given adsorption properties.

Despite many attempts at a theoretical analysis of the phenomenon of physical adsorption of gases and vapors, until now there has been no theory that described quantitatively the adsorption equilibrium for actual porous adsorbents over a wide range of temperatures and pressures. Moreover, even for a given adsorbent, none of the existing theories make it possible to predict the adsorption equilibrium on the basis of known characteristics of the adsorbent and substance adsorbed. The only exception is the potential theory of adsorption, which Polanyi began and which was developed in our laboratory. In its present state, this theory makes it possible to solve the main problems of adsorption equilibrium over a wide range of parameters and with a high accuracy, which is at least adequate for practical purposes [1-7].

In the report I will attempt to formulate the main ideas of the theory and demonstrate its applicability to various adsorbents which are of great technical importance. E. D. Zaverina, L. V. Padushkevich, D. P. Timofeev, K. M. Nikolaev, B. P. Bering, V. V. Serpinskii, B. A. Vas'kovskii, E. G. Zhukovskaya, and B. N. Vasil'ev played a major part in the experimental and theoretical investigations.

Bases of the theory of physical adsorption of gases and vapors. In physical adsorption, which is caused by dispersion forces, the porous structure of the adsorbents has a substantial effect on the adsorbability of substances. The fields of adsorption forces created by opposite walls of the pores overlap in the finest pores of adsorbents or micropores, whose dimensions are comparable in order of magnitude to the dimensions of the molecules adsorbed. As a result, in such pores there is an increase both in the adsorption potentials and in the differential heats of adsorption, due to which there is a considerable increase in the amounts of adsorption. We consider such adsorbents as being of the first structural type [2]. For adsorbents of the second structural type with coarser pores, there is practically no increase in adsorption potentials and they differ in adsorption properties from non-porous adsorbents largely due to the difference in specific surface [2]. Adsorbents consisting of nonpolar substances, mainly carbonaceous adsorbents, were particularly suitable for experimental testing of the main premises of the theory of adsorption due to the determining role of the dispersion forces in the adsorption interaction.

Even in the early years Polanyi showed that at relatively low temperatures, the so-called characteristic curves which show the relation of the volume of adsorption space filled with condensed vapor to the corresponding potential, which are readily calculated from vapor adsorption isotherms, are practically independent of temperature [8,9]. This basic premise of the potential theory of adsorption has been developed further in our investigations.

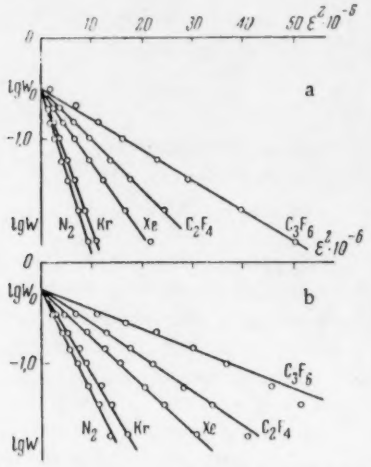

Fig. 1. Characteristic adsorption curves in the linear form according to equation (1) : a) AC-1; b) for AC-2.

On the basis of a large amount of experimental material and theoretical considerations, it was established that the characteristic curve of an adsorbent gives the distribution of filled volumes of the adsorption space W with respect to the adsorption potentials ϵ, where this distribution depends on the microporous structure of the adsorbents. For adsorbents of the first structural type, the characteristic equation has the form

$$W = W_0 e^{-k\epsilon^2/\beta^2} \qquad (1)$$

and for adsorbents of the second structural type

$$W = W'_0 e^{-m\,\epsilon/\beta} \qquad (2)$$

In these equations, W_0 and W'_0 are the limiting volumes of the adsorption space and β is the affinity coefficient, which allows for the nature of the vapor adsorbed.

As adsorption occurs within the volume of the adsorption space limited by the walls of the micropores for adsorbents of the first structural type, the limiting volume of the adsorption space W_0 in this case expresses the volume of the micropores of the adsorbent. Figure 1 gives in a linear form the characteristic adsorption equations (1) for two samples of activated carbons of the first structural type which differ sharply in microporous structure [4]. The experimental points calculated from the adsorption isotherms for different termperatures lie satisfactorily on straight lines, which serves as a check between the agreement between the characteristic equation and experimental data. Moreover, for each active carbon, the lines for different substances intersect the ordinate axis at one point. This indicates the constancy of the limiting volumes of the adsorption space or the volumes of the micropores for each carbon. Allowance for the affinity coefficients which are independent of the porous structure of the active carbons, and appear in the slopes of the lines, makes it possible to reduce the lines for different substances to one line, corresponding to the chosen standard substance.

Figure 2 shows in the linear form the characteristic equation (2) for adsorbents of the second structural type for the system silica gel – carbon dioxide [5]. The experimental points correspond to isotherms for wide ranges of temperature and pressures. This equation also agrees with experimental data.

The change from the amounts of adsorption a to the filled volumes of the adsorption space W and from equilibrium relative pressures p/p_s to the adsorption potentials ϵ is of particular importance in the potential theory of adsorption. The filled volume of the adsorption space may be expressed as the product of the amounts of adsorption in moles/g and the molar volume of the substance in the adsorbed state v^* in cc/mole:

$$W = av^* \qquad (3)$$

According to Polanyi, at relatively low temperatures, v^* may be taken as equal to the molar volume of the substance for the bulk liquid phase, i.e.,

$$v^* = v \qquad (4)$$

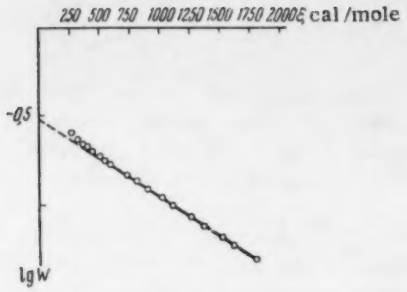

Fig. 2. Characteristic curve in a linear form according to equation (2) for the adsorption of carbon dioxide on silica gel.

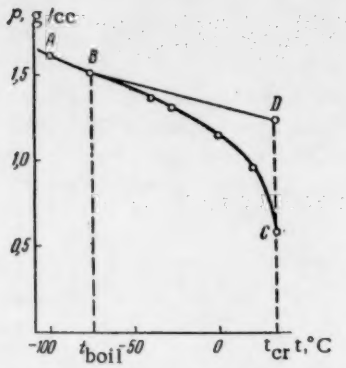

Fig. 3. Temperature dependence of the density of liquid tetrafluoroethylene.

According to our investigations, this is justified for temperatures below the boiling point of substances at atmospheric pressure. Over the range of temperatures from the boiling point to the critical temperature for the bulk liquid phase, there is a considerable decrease in the density as the critical temperature is approached and this is shown by the curve BC in Fig. 3 for tetrafluoroethylene. In parallel, there is a sharp increase in the compressibility of the liquid. Since an adsorbed substance in micropores is in a strongly compressed state, its density is considerably greater and according to our investigations, may be expressed by the line BD. The point B on this line at the boiling point corresponds to the tabular value of the density, while the point D at the critical temperature corresponds to a density equal to four times the true volume of the molecules, i.e., the constant b in the van der Waals equation [4,5]. The molar volumes for the densities interpolated from the line BD were previously denoted by v^*. For temperatures above the critical temperatures:

$$v^* = b, \tag{5}$$

i.e., the molar volume of the adsorbed substance corresponds to the maximum compression of the gas. This is correct only for adsorbents of the first structural type, into whose micropores a small number of adsorption layers fit so that the fields of the opposite walls of the pores overlap.

From our investigations [4,5] it follows directly that for temperatures below or equal to the critical temperature, the adsorption potential calculated by Polanyi's formula [8,9]

$$\epsilon = 2.30\ RT \lg p_s / p, \tag{6}$$

expresses the differential molar work of adsorption with the initial state corresponding to the saturated vapor. Correspondingly, for the gaseous state of the substance we obtained [4]:

$$\epsilon = 2.30\ RT \lg \tau^2\ p_{cr}/p, \tag{7}$$

where p_{cr} is the critical pressure and

$$\tau = \frac{T}{T_{cr}} \tag{8}$$

is the reduced temperature. When $T = T_{cr}$ and $p_{cr} = p_s$, $\tau = 1$ and formula (7) becomes (6).

An example of the experimental proof of the relations examined is the characteristic curve for the adsorption of xenon on active carbon illustrated in Fig. 4. It was calculated from the xenon adsorption isotherms for the temperature range from -107 to 50°, which covers the vapor and gaseous states of the substance (t_{cr} = 16.6°). The fact that the experimental points lie on the same curve confirms the method presented for calculating W and ϵ. The characteristic curve in Fig. 4 agrees well with equation (1) and was given in the linear form in Fig. 1.

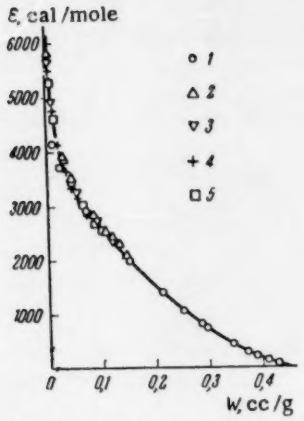

Fig. 4. Characteristic curve for the adsorption of xenon on AC-1, calculated from the adsorption isotherms: 1) at -107°; 2) at 0°; 3) at 16.6° (cr); 4) at 30°; 5) at 50°.

Thermal adsorption equations and equations of the adsorption isotherms for adsorbents of the limiting structural types may be obtained readily from equations of the characteristic curves (1) and (2) and formulas (3), (5), (6), and (7), which express the filled volumes of the adsorption space in terms of the amount of adsorption and, respectively, the adsorption potentials in terms of the equilibrium relative pressures.

Adsorbents of the first structural type

Gases $T \geq T_{cr}$

$$a = \frac{W_0}{b} e^{-B T^2/\beta^2 (\lg \tau^2 p_{cr}/p)^2}. \quad (9)$$

Vapors $T \leq T_{cr}$

$$a = \frac{W}{v^*} e^{-B T^2/\beta^2 (\lg p_s/p)}, \quad (10)$$

Whereby when $T < T_{boil}$, $v^* = v$ (tabular value of the molar volume). Equations (9) and (10) apply over the range of filling of the adsorption space W/W_0 from 0.06 to 0.94.

Adsorbents of the second structural type

Vapors $T \leq T_{cr}$

$$a = \frac{W_0'}{v^*} e^{-A T/\beta \lg p_s/p}. \quad (11)$$

Equations (9) and (11) are equations of adsorption isotherms, but in the implicit form they are thermal adsorption equations. If tabulated values of the saturated vapor pressure are used and the molar volumes v^* are found as was considered above, then it is possible to calculate the amounts of adsorption for any given temperatures.

Finally, according to the theory of dispersion forces, from the expression for the adsorption potential it is possible to obtain a simple, approximate formula for the affinity coefficients of the characteristic curves [10]

$$\beta = \frac{P}{P_0} \quad (12)$$

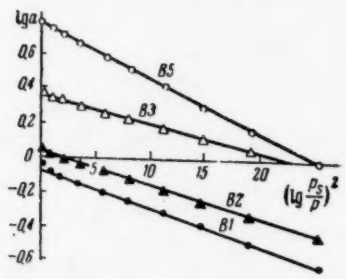

Fig. 5. Adsorption isotherms for benzene vapor at 20° in the linear form according to equation (10) for samples of active carbons from sucrose of series B.

where P is the parachor of the substance examined and P_0 is the parachor of the standard substance, from whose adsorption isotherm the constants W_0 and B or W'_0 and A of the adsorption isotherm equations were determined. The parachors of substances may be regarded as the molar volumes of the substances in the liquid state reduced to the same internal pressures and are approximately proportional to their polarizability coefficients.

The temperature independence of the characteristic equations makes it possible to use a thermodynamic method of calculating differential heats of adsorption as a function of the amount of adsorption. In this way the following equations were obtained [11,12] for adsorbents of the first structural type

$$q = \frac{2.3^{\frac{1}{2}} \alpha \beta RT}{2B^{\frac{1}{2}}} \left(\lg \frac{W_0}{av}\right)^{-\frac{1}{2}} + \frac{2.3^{3/2} \beta R}{B^{\frac{1}{2}}} \left(\lg \frac{W_0}{av}\right)^{\frac{1}{2}} \quad (13)$$

and for adsorbents of the second structural type

$$q = \frac{2.3\,\alpha RT}{A} - \frac{2.3^2 \beta R}{A} \left(\lg \frac{av}{W'_0}\right), \quad (14)$$

where q is the purely differential heat of adsorption (the difference between the total differential heat of adsorption and the latent heat of condensation) and α is the thermal coefficient of cubic expansion of the adsorbed substance.

Application of the theory to the quantitative description of adsorption equilibria. The experimental data presented in Figs. 1, 2, and 4 indicate that the theory is readily applicable to the adsorption of gases and vapors on carbonaceous adsorbents. For a clearer representation, Fig. 5 gives in the linear form isotherms for the adsorption of benzene vapor (10) on a number of active carbon samples, which differ sharply in adsorption properties and microporous structure [1]. Equation (10) describes the experimental data over a wide range of equilibrium relative pressures from $p/p_s = 1 \cdot 10^{-5}$ to 0.1, i.e., over a range of four orders of magnitude. Figures 1 and 4 show how well the temperature dependence of adsorption is expressed.

The approximate expression for the affinity coefficient (12) as the ratio of the parachors of the substances also agrees quite well with experimental data. The table gives typical results of a comparison of the calculated and experimental values of the affinity coefficients for carbonaceous adsorbents [6, 7]

TABLE. Calculated and Experimental Values of Affinity Coefficients. Standard vapor benzene ($\beta = 1$)

Vapor material	β exp	$\beta = \frac{P}{P_0}$
Benzene	1.00	1.00
Nitrogen	0.33	0.34
Methyl bromide	0.57	0.60
Ethyl chloride	0.71	0.72
Propane	0.72	0.73
n-Butane	0.87	0.92
Chloroform	0.87	0.89
Carbon tetrachloride	0.96	1.07
n-Pentane	1.08	1.11
n-Hexane	1.29	1.29
n-Heptane	1.46	1.48

Figure 6 shows the applicability of the adsorption isotherm equation (11) to active carbons of the second structural type [2].

On the whole, the adsorption theory presented makes it possible to use the structural constants W_0 and B or W'_0 and A, respectively, determined from the adsorption isotherms of a standard vapor on carbonaceous adsorbents, to calculate with sufficient accuracy for practical purposes the adsorption equilibria for various gases and vapors over wide ranges of temperature and pressures solely on the basis of the physical constants of the substances adsorbed. By means of equations (13) or (14), from these constants it is also possible to calculate the differential heats of adsorption of various vapors for amounts of adsorption and temperatures lying within the limits of applicability of the adsorption isotherm equations (10) and (11).

The basic premises of the adsorption theory also remain accurate for mineral adsorbents, for example, dehydrated inorganic gels, natural adsorbents, etc., for the adsorption of vapor of apolar substances when the dispersion component plays the determining role in the adsorption interaction. As an example, Fig. 7 shows in the linear form adsorption isotherms for benzene vapor according to equation (10) for finely porous silica gel and according to equation (11) for coarsely porous silica gels [13].

In recent years we have studied the adsorption properties of dehydrated synthetic zeolites or so-called molecular sieves. In these adsorbents, the main volume of the adsorption space consists of elementary hollows, formed after dehydration in the crystalline structure of sodium or potassium aluminosilicates, the access to which is limited by narrower entrances or "windows". Zeolites adsorb well only those substances whose molecules are capable of passing through the window into the hollow. The adsorption power of zeolites for substances with larger molecules, for which the windows are impassable, is insignificantly small over a wide range of relative pressures.

The inner elementary hollows of zeolites with dimensions of the order of molecular dimensions may be regarded as micropores. In this case, zeolites should be adsorbents of the first structural type as in the physical adsorption of vapor of apolar substances there will be a sharply expressed increase in adsorption potentials. In actual fact, adsorption isotherms for vapors whose molecules are capable of penetrating the windows of the micropores are well expressed by the adsorption isotherm equation of the first structural type. Figure 8 shows in the linear form of equation (10) isotherms for low-temperature adsorption of nitrogen and argon vapor both according to our data [14] and according to the experiments of Barrer and Robins [15] for synthetic and natural zeolites.

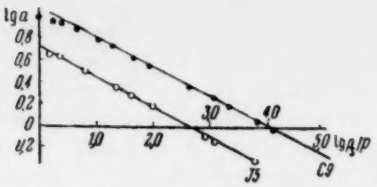

Fig. 6. Adsorption isotherms for benzene vapor at 20° in the linear form according to equation (11) for active carbon samples C-9 and J-5 of the second structural type.

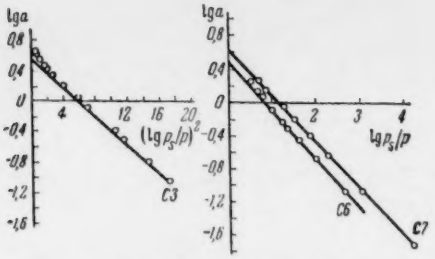

Fig. 7. Adsorption isotherms for benzene vapor at 20° in the linear form according to equation (10) for finely porous silica gel C-3 according to equation (11) for coarsely porous silica gels C-6 and C-7.

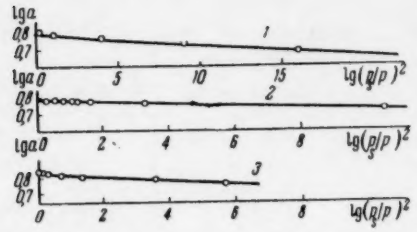

Fig. 8. Adsorption isotherms in the linear form according to equation (10) for: 1) nitrogen vapor at -195° on Linde molecular sieve 5A [14]; 2) nitrogen vapor at -183° on chabazite [15]; 3) argon vapor at -183° on chabazite [15].

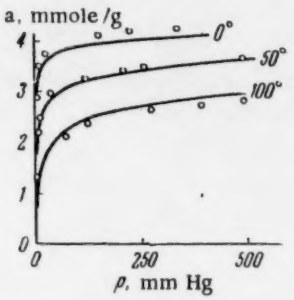

Fig. 9. Isotherms for the adsorption of methyl chloride vapor on natural chabazite at various temperatures.

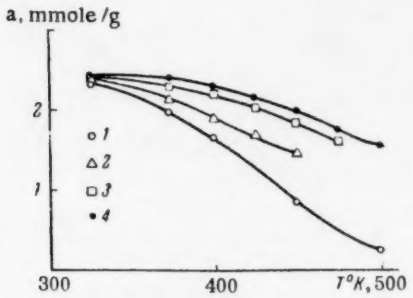

Fig. 10. Isobars for the adsorption of n-hexane vapor on a molecular sieve of type 5A for various equilibrium pressures p in mm Hg: 1) p = 0.5; 2) p = 5; 3) p = 50; 4) p = 100.

The possibilities of theoretical prediction of adsorption equilibria for the precritical region are illustrated by isotherms for the adsorption of methyl chloride vapor on natural chabazite for various temperatures, calculated from the adsorption isotherm equation (10) and shown by solid curves in Fig. 9 [14]. The circles show experimental points from the experiments of Barrer and Brook [16]. The basis of the calculations was the adsorption isotherm for nitrogen vapor on chabazite at -183° [15], from which the constants W_0 and B were found for nitrogen as the standard vapor. Apart from this, we used only the physical constants of the substances. The deviation between the calculated values and experimental data did not exceed 5 %.

Finally, Fig. 10 showsisobars for the adsorption of n-hexane vapor at various equilibrium pressures on a molecular sieve of the type 5A, synthesized by Ya. V. Mirskii, from the author's measurements. According to equation (10)

$$\lg av^{\bullet} = \lg W_0 - 0.434 \frac{B}{\beta^2} [T \lg p_s/p^2] \qquad (15)$$

and, consequently, the experimental points of all the isobars in the coordinates $\lg av^{\bullet} - [T \lg P_s/P]^2$ should lie on one straight line. The graph in Fig. 11 shows that this result of the adsorption theory is justified quite satisfactorily by experiment right up to the critical temperature of n-hexane.

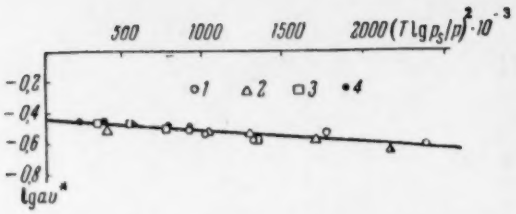

Fig. 11. Isobars for the adsorption of n-hexane vapor on molecular sieve of type 5A in the linear form according to equation (15) for various equilibrium p in mm Hg: 1) at p = 0.5; 2) at p = 5; 3) at p = 50; 4) at p = 100.

Thus, the potential theory of adsorption of gases and vapors developed in our laboratory describes adsorption equilibria quite satisfactorily for adsorbents of various natures over wide ranges of temperature and pressure with the condition that dispersion forces play the determining role in the adsorption interaction.* The theory makes it possible to predict adsorption equilibria and determine the differential heats of adsorption solely on the basis of physical constants of the substances adsorbed. The calculation method of the theory is of practical importance in solving a number of problems in sorption technology.

SUMMARY

1. The present state of the potential theory of adsorption of gases and vapors developed in the laboratory of sorption processes of the Institute of Physical Chemistry, Academy of Sciences, USSR, is presented.

2. The possibilities of the theory for describing and predicting adsorption equilibria and differential heats of adsorption are demostrated.

3. The theory is applicable to the adsorption of gases and vapors on adsorbents of various chemical natures and porous structures with the condition that the dispersion component plays the determining role in the adsorption interaction.

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* An increase in the relative role of the electrostatic components of the adsorption interaction increases the affinity coefficient β compared to the value calculated from formula (12).

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CATALYTIC CONVERSIONS OF SOME ALKYL HALIDES

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While the kinetics and mechanism of the thermal decomposition of alkyl halides has attracted the attention of many investigators [1-13], the catalytic conversions of alkyl monohalides have been studied little. We investigated the catalytic decomposition of 2-chloropropane and some alkyl bromides in the presence of α-Fe, Fe_2O_3, and mixed $Fe_2O_3 \cdot Cr_2O_3$ (1 : 1) catalysts.

EXPERIMENTAL

The kinetic experiments were carried out by a flow method on the catalytic apparatus adopted in our laboratory. Some series of experiments were carried out with a differential thermocouple on a PK-52 photorecording pyrometer. Standard catalysts were prepared from nitrates by precipitation with 2 N sodium hydroxide solution, washed until a test for NO_3^- was negative, formed, dried at up to 110°, loaded into the catalyst tube as a bed of 1.2-1.5 cm, and treated with air at 425° for 7 hr. The α-Fe was obtained by reduction of the oxalate with electrolytic hydrogen (3 liter/hr/5 ml) for 6 hr at 450°. The alkyl halide was introduced into the reaction space automatically at a given rate. The gaseous reaction products entering the eudiometer passed through a titration solution of alkali for trapping the hydrogen halide. The gas volume was read off every minute. The gas volume (n.p.t.) liberated in 3 min was taken as a measure of the catalytic activity of the catalyst. The experimental percent conversion was calculated on the unsaturated hydrocarbons and checked by the alkali titer. A preliminary pyrolysis of the starting materials was carried out and this showed that thermal decomposition of alkyl halides is observed at higher temperature than catalytic decomposition.

Table 1 gives the constants of the starting materials.

TABLE 1
Physical Constants of Alkyl Halides Used

Name	Boiling point in °C		d_4^{20}		n_D^{20}	
	Experimental data	Literature data	Experimental data	Literature data	Experimental data	Literature data
2-Chloropropane	36	36	0.8641	0.859	1.3781	1.3784
Bromoethane	37	38	1.4550	1.4555	1.4230	1.4238
Bromopropane	70.5	70.8	1.3541	1.3529	1.4348	1.43414
2-Bromopropane	60	59	1.3102	1.3097	1.4256	1.4250
2-Bromobutane	91.5	90-93	1.2510	1.2507	1.4352	1.4344
2-Bromo-2-methylpropane	73	72	1.2126	1.2220	1.4282	1.4280

Catalytic conversions of 2-chloropropane. Figure 1 shows the decomposition rate of 2-chloropropane on $Fe_2O_3 \cdot Cr_2O_3$ at a constant input rate of the material of 0.15 ml/min. As Fig. 1, a, shows there was uniform liberation of gas over a period of 60 min, indicating that the catalyst retained its activity under the experimental conditions. Table 2 gives results of kinetic experiments on a mixed Fe—Cr catalyst (1:1) over the range 250-290°.

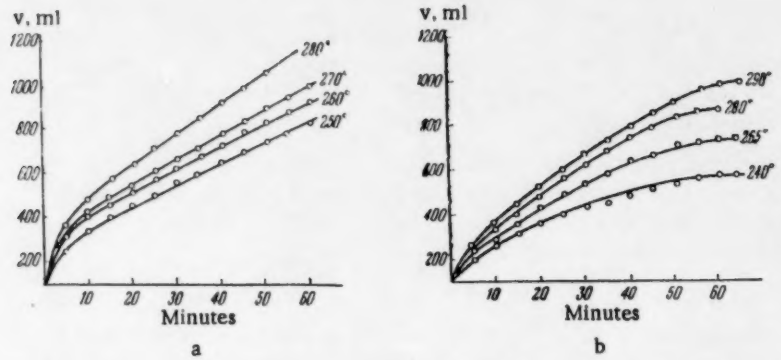


Fig. 1. Decomposition rate of 2-chloropropane on $Fe_2O_3 \cdot Cr_2O_3$ (1 : 1) (1, a) and on the the same catalyst after $(CH_3)_2CHOH$ (1, b).

TABLE 2

Catalytic Decomposition of 2-Chloropropane;(rate 0.13 ml/min; time 55 min; catalyst volume 5 ml; layer 1.2 cm; diameter 2 mm)

Temperature in °C	v in ml/min n.p.t.	Gas analysis			Degree of conversion on C_nH_{2n} in %	n_D^{20}
		C_nH_{2n}	H_2	C_nH_{2n+2}		
		Fe_2O_3 ε = 15,2 kcal/mole				
270	9,7	95,0	2,7	2,3	28,2	1,3785
280	12,3	93,5	3,0	3,5	34,5	1,3787
290	17,7	93,0	4,0	3,0	50,3	1,3790
300	20,3	91,5	4,0	4,5	56,8	1,3788
290	17,5	93,5	3,5	3,0	50,3	1,3786
320	28,7	91,2	4,0	4,8	80,3	1,3790
		Cr_2O_3 ε = 13,3 kcal/mole				
200	6,7	96,0	2,4	1,6	19,6	1,3785
210	9,2	97,2	2,0	0,8	27,3	1,3787
220	12,6	96,3	2,0	1,7	31,2	1,3791
220	12,5	97,2	1,0	1,8	31,0	1,3792
230	14,8	96,8	2,2	1,0	43,8	1,3789
210	9,5	97,0	2,0	0,8	28,1	1,3784
		$Fe_2O_3 \cdot Cr_2O_3$ (1 : 1) ε = 11,8 kcal/mole				
220	6,0	96,9	1,0	2,1	17,8	1,3781
230	7,2	97,0	1,0	2,0	21,3	1,3784
240	9,6	97,0	1,2	1,8	28,4	1,3785
250	13,1	96,2	1,4	2,4	41,3	1,3789
260	15,2	97,0	1,0	2,0	45,0	1,3783
270	18,4	96,4	1,6	2,0	54,6	1,3784
270	18,2	96,5	0,5	3,0	54,3	1,3783
280	19,4	97,0	1,2	1,8	57,5	1,3786
290	22,3	95,0	2,0	2,8	64,8	1,3792
290	22,6	95,6	1,8	2,6	65,4	1,3791

The reproducibility of the results was satisfactory. The decomposition resulted in the formation of unsaturated hydrocarbons, hydrogen chloride, and traces of C_nH_{2n+2} (up to 2.5-3%). In all experiments the catalyzate was pale yellow and acid to Congo red. After treatment with sodium carbonate solution, it was dried and fractionated to yield the starting 2-chloropropane. No other substances were detected.

From the experimental data we calculated the apparent activation energy ε, which equalled 11.8 kcal per mole. It was observed that if the catalyst was first treated with isopropyl alcohol at 340-400°, its activity in the decomposition of alkyl halide fell continuously during one working cycle as is shown by Fig. 1, b. The activity of the catalyst could be restored by regeneration with air, but after 15-20 min the gas liberation rate decreased and the reaction stopped. Fresh catalyst was therefore used in the reaction.

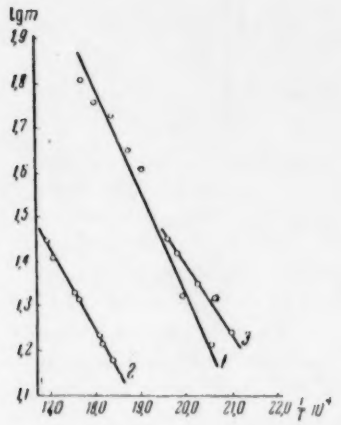


Fig. 2. Relation of log m to $1/T \cdot 10^4$ for the decomposition of 2-chloropropane on $Fe_2O_3 \cdot Cr_2O_3$ (1:1)(1); Cr_2O_3 (2); Fe_2O_3 (3).

Table 2 also gives the results of experiments on chromium oxide and iron oxide. The decomposition of 2-chloropropane on chromium oxide (input rate 0.13 ml/min) occurred at lower temperatures (200-230°) and yielded hydrogen chloride and unsaturated hydrocarbons. The experimental data was used to calculate the activation energy, which equalled 13.3 kcal/mole. The decomposition of 2-chloropropane on iron oxide occurred at 270-320° and yielded propylene and HCl, but was considerably complicated by the formation of methane. The apparent activation energy equalled 15.2 kcal/mole. Figure 2 shows the relation of the logarithm of the degree of conversion, expressed in percent of 2-chloropropane, calculated on unsaturated hydrocarbons, to the reciprocal absolute temperature.

Catalytic conversions of alkyl bromides. We studied the catalytic decomposition of bromopropane, 2-bromopropane, 2-bromobutane, and 2-bromo-2-methylpropane in the presence of Fe_2O_3 and $Fe_2O_3 \cdot Cr_2O_3$ (1 : 1) under identical conditions. The amount of catalyst was 5 ml (ϕ 0.2 mm), the layer was 1.5 cm, and the input rate 0.175 ml/min. Dilution with nitrogen (1.5-2 liter/hr) was used in a series of experiments. As this table shows, the decomposition temperatures of alkyl bromides differ and depend on the structure of the radical; bromopropane decomposes at 280-320°, while 2-bromobutane decomposes at 340-380°, which agrees with the observations of Senderen [14]. It should be noted that the decomposition temperature increases in relation to the number of carbon atoms and their steric arrangement; the more branched tert-butyl bromide decomposes at a much higher temperature than sec-butyl bromide. The decomposition mechanism is complex and is not first order. In all cases, the catalytic decomposition resulted in the formation of unsaturated hydrocarbons and hydrogen halide; this was accompanied by cracking of the hydrocarbon molecule with liberation of saturated hydrocarbons and hydrogen. It was observed that cracking increased with branching of the hydrocarbon radical of the alkyl bromide and reached 18-20% for 2-bromo-2-methylpropane.

The decomposition on iron oxide occurred at somewhat higher temperatures than on $Fe_2O_3 \cdot Cr_2O_3$, but with a lower percent conversion (calculated on unsaturated hydrocarbons) as there was considerable methane formation and hydrogen liberation. Combining the iron oxide with chromium oxide increased the percent of unsaturated hydrocarbons, but did not completely eliminate the cracking effect of iron oxide.

The degree of conversion on the alkyl bromide passed differed in all cases, but did not exceed 32%. In all cases, the refractive index of the catalyzate ($n_D^{t^0}$) changed insignificantly. Fractionation of the catalyzate showed that it contained the starting alkyl bromides, but no isomerization products were isolated. We studied the reverse reaction, i.e., the catalytic reaction of propylene with gaseous HBr at various space velocities on spent catalysts over a wide temperature range, but did not observe the formation of alkyl bromides. Special additions of $MeCl_2$ to the catalyst also gave negative results. Thus, the retarding stage of the catalytic decomposition of alkyl halides is the desorption of HBr. The accumulation of hydrogen halide reduced the decomposition rate and decomposition practically ceased after catalysis for 35-40 min. Dilution with nitrogen did not affect the working life of the catalyst. Consequently, the change in the degree of conversion and the change in the apparent activation energy are not connected with a change in the direction of the reaction.

TABLE 3

Results of Experiments on the Catalysis of Alkyl Bromides

Substance	$Fe_2O_3 \cdot Cr_2O_3$ (1 : 1)				Fe_2O_3				Thermal decomp.	
	temperature range in °C	yield on C_nH_{2n} in %	ε in kcal/mole	E in kcal/mole	temperature range in °C	yield on C_nH_{2n} in %	ε in kcal/mole	E in kcal/mole	ε in kcal/mole	lit. ref.
Bromopropane	280—320	17—34	12,8	17,1	300—330	19—26	11,5	15,3	50,7 42,0	32 34
2-Bromopropane	240—270	11—38	15,9	21,2	260—290	11—31	18,3	24,4	47,8 47,0	32 34
2-Bromobutane	340—380	6—42	19,4	23,2	370—400	12,6—26,3	21,2	28,3	43,8 45,6	33 34
2-Bromo-2-methylpropane	490—520	17,5—22	21,7	28,9	500—520	13—16,5	—	—	42,2 48,0	33 34

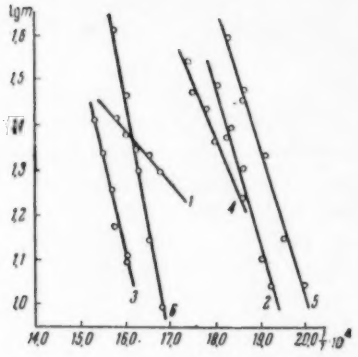


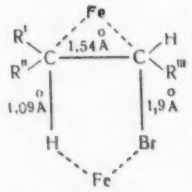
Fig. 3. Relation of log m to $1/T \cdot 10^4$ for the decomposition of some alkyl bromides:

	Fe_2O_3	$Fe_2O_3 \cdot Cr_2O_3$ (1:1)
Bromopropane	1;	4
2-Bromopropane	2;	5
3-Bromobutane	3;	6

Figure 3 shows the relation of the logarithm of the degree of conversion on unsaturated hydrocarbons to the reciprocal temperature ($1/T \cdot 10^4$). The points lie satisfactorily on straight lines from which it is possible to calculate ε, i.e., the apparent activation energy of catalytic decomposition of alkyl halides on $Fe_2O_3 \cdot Cr_2O_3$ and Fe_2O_3. As Table 3 shows, the values of ε differ and increase in relation to the structure of the alkyl halide and this shows in the values of E, i.e., the energy barrier of the reaction. From a comparison with literature data for ε for the thermal decomposition of alkyl bromides (last column) it follows that ε for catalytic decomposition is considerably less.

In the present work we followed the process by means of a differential thermocouple [15] with a photographic recorder. Figure 4 shows differential curves obtained on a PK-52 with a chromel-alumel thermocouple (thermocolumn), consisting of 20 junctions. With an increase in the temperature of 2-bromopropane decomposition on Fe_2O_3, there was an increase in the degree of conversion, which showed as an increase in the exothermal effect on the differential curve (left-hand part of Fig. 4). As the catalyst was regenerated between experiments with air at temperatures above 350°, the hermograms showed a second large exothermal wave (right-hand part of Fig. 4). As chemical analysis showed, at this point there was oxidation of HBr by atmospheric oxygen with the formation of bromine, which reacted with the catalysts. It was found that spent catalysts became acidic and contained ferric bromide. TiO_2 is known to be inert to acids and gaseous HCl and HBr. 2-Bromopropane was decomposed on a mixed $Fe_2O_3 \cdot TiO_2$ (1:1) catalyst at 320°. Chemical analysis showed that the spent catalyst contained ferric bromide, while the TiO_2 remained unchanged.

According to the multiplet theory [16], the catalytic process proceeds through an intermediate complex, which is formed by the superposition of the index group of the molecule on active centers of the catalyst. The rate of the catalytic reaction is determined by the properties of this intermediate complex. The decomposition index of an alkyl bromide on the catalyst may be represented in the following general form:



where the outer substituents R', R", and R''' are radicals or hydrogen.

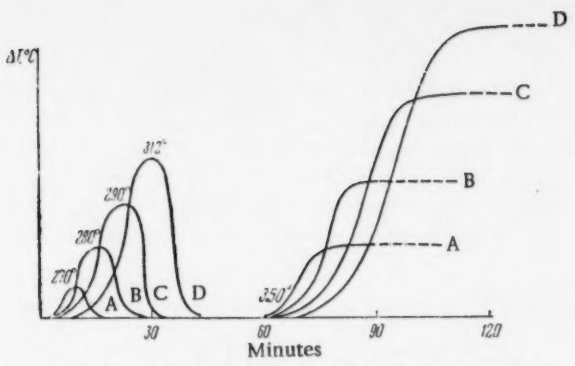


Fig. 4. Differential thermogram of the decomposition of 2-bromopropane on Fe_2O_3.

The outer substituents may affect the index group of the molecule $\rangle C-C\langle$ (H, Br). In polar compounds like alkyl bromides they may cause displacement of electron density and deformation of the molecule, which changes the distance between the atoms of the index group. This appears both as a change in individual bonds in the molecule itself and as a change in the energy of the bromine–catalyst bond. The localization of electron density of a bromine atom should affect the rate of catalytic conversion. In addition, the outer substituents shield the index group, promote cracking of the hydrocarbon part of the molecule, and hamper the main direction of the process. All this is reflected in the values of the activation energy. However, the differences in ε we found are so great that they cannot be explained solely by the effect of the structure of the reacting alkyl bromide molecules. The specific action of the catalysts must also be considered.

In our work [17] it was shown that the mechanism of the action of a mixed iron–chromium catalyst (1:1) appears at the boundary of the two solid phases, iron oxide and chromium oxide, which retain their individuality at temperatures up to 500°, as was demonstrated by x-ray analysis. It seems to us that when the C–C bond of the index group is superposed on the active center of iron at the boundary of the two phases, rupture of this bond occurs, i.e., cracking of the hydrocarbon part (radical) of the molecule is observed. If it is assumed that cracking of normal alkyl bromides may proceed in one direction, while cracking of isoalkyl bromide may occur in two or three directions, then the increase in the amount of saturated hydrocarbons and hydrogen (cracking products) in the series n-propyl bromide–tert-butyl bromide becomes understandable.

A study of the catalytic conversions of alkyl halides in the presence of α-Fe is of particular interest. On the one hand, it is known [18-22] that iron does not give organometallic compounds of the type R_2FeHal or $RFeHal_2$, containing Fe^{2+} or Fe^{3+}, but tends to form organic complexes [23, 24]. On the other hand, at high temperatures, the reaction of body-centered cubic iron with saturated hydrocarbons [25] or isopropyl alcohol [26] forms low-temperature carbides Fe_2C and Fe_3C, whose crystal lattices are not ionic but inclusion structures [27].

There arises the problem of the nature of the intramolecular forces and the magnitude of the energy of the Fe–C bond in these compounds. The value of Q_{Fe-C} has not yet been determined by any available method [28]. An attempt to solve this problem by the kinetic method [29] proposed by one of us has been unsuccessful as yet as when the reaction is carried out with the index $\rangle C-C\langle$ (H, H) there is extensive cracking of the reacting molecule with the introduction of carbon into the iron lattice at low temperature or the formation of carbon which is neutral to x-rays at temperatures of $\sim 400°$. According to the work of Kiperman and one of us [30], the calculated value of Q_{Fe-C} equals 19.1 kcal/mole.

It was very tempting to investigate the interaction of C_2H_5Br and C_3H_7Br with active α-Fe over a wide temperature range, from 0 to 400°, the more so as an article [30] appeared in 1952 in which the synthesis of a compound of the type interesting us was reported. The synthesis of $(C_2H_5)_2FeBr$ or $C_2H_5FeBr_2$ would make it possible to determine the value of Q_{Fe-C} thermochemically or spectroscopically. In experiments carried out to achieve this reaction, we investigated active α-Fe, obtained from iron oxalate by reduction with hydrogen or by its decomposition in an inert gas atmosphere. We varied the reaction conditions, the nature of the solvents (ethers, esters, dioxane, acetone, and other ketones), the temperature (from -5 to 100°), and the heating time. Many experiments showed that α-Fe does not form compounds similar to a Grignard reagent and prolonged heating gives insignificant amounts of ferric bromide.

Catalytic conversions of C_2H_5Br and C_3H_7Br were observed at high temperatures (from 180-400°) in the vapor phase. The decomposition of alkyl halides in the presence of α-Fe was accompanied by the formation of HBr, unsaturated and saturated hydrocarbons, and hydrogen. Very small amounts of ferric bromide were formed,

but there was no formation of carbides as demonstrated by thermomagnetic [31] and x-ray analyses. X-ray analysis showed that the spent catalysts contained α-Fe (a = 2.86 A), whose lattice coincided with that of Armco iron (99.6%) and did not contain other crystalline impurities.

SUMMARY

1. A study was made of the catalytic decomposition of 2-chloropropane and a number of normal and iso-alkyl bromides in the presence of the catalysts α-Fe, Fe_2O_3, and Fe_2O_3–Cr_2O_3 (1:1). The decomposition of alkyl halides resulted mainly in the formation of hydrogen halide and unsaturated hydrocarbons and a change from n-C_3H_7Br to C_4H_9Br did not alter the direction of the process, but it occurred at different temperatures over the range 200-400° with different percent conversions. The decomposition process was complicated by cracking of the starting materials and the formation of surface compounds of iron halide, whose presence was demonstrated by chemical analysis.

2. We determined the apparent activation energies for the decomposition of alkyl halides under conditions found as a result of the present investigation.

3. An attempt to prepare an organometallic compound of the type R_2FeHal or $RFeHal_2$ was unsuccessful.

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EFFECT OF HYDROGEN PRESSURE ON THE RATE OF HETEROGENEOUS CATALYTIC ISOMERIZATION OF CYCLOHEXANE

COMMUNICATION 3. ANALYSIS OF THE REASONS FOR THE RETARDATION OF CYCLOHEXANE ISOMERIZATION AT A HIGH HYDROGEN PRESSURE

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Our investigation [1, 2] of the isomerization of cyclohexane to methyl cyclopentane in the presence of an industrial WS_2 catalyst in a flow system showed that in the kinetic region (up to 380°) there is a considerable decrease in the reaction rate constant with an increase in the partial hydrogen pressure from 50 to 250 atm; this effect decreased as the temperature was raised from 320 to 380°. The retardation of heterogeneous catalytic isomerization of cyclohexane with an increase in hydrogen pressure could be caused by various factors: a) displacement of the adsorption equilibrium of cyclohexane under the effect of hydrostatic pressure; b) a decrease in the adsorption of cyclohexane as a result of covering of the catalyst surface by adsorbed hydrogen; c) the specific role of hydrogen in cyclohexane isomerization.

In the present work we attempted to analyze these three possible reasons for the effect of hydrogen pressure and this necessitated some additional experimental investigations.

EXPERIMENTAL

Catalytic isomerization of cyclohexane under a nitrogen-hydrogen pressure. From the work of Krichevskii and Kal'varskaya [3] and Temkin [4] it follows that the amount of gas(vapor)adsorbed from a mixture increases with an increase in pressure only until its partial molar volume over the adsorbent exceeds the partial molar volume of the adsorbate. These volumes become equal at a certain pressure and this corresponds to the adsorption maximum. A further increase in pressure leads to a decrease in the amount of adsorbed substance. Krichevskii and Kal'varskaya showed that the adsorption maximum of benzene and carbon tetrachloride vapor on activated carbon at 50° at a pressure of hydrogen, nitrogen, and a nitrogen-hydrogen mixture occurs at a pressure somewhat below 100 atm. In this case, the role of hydrogen, nitrogen and the nitrogen-hydrogen mixture is reduced to creation of hydrostatic pressure.

If it is assumed that the adsorption maximum of cyclohexane on tungsten sulfide occurs in the lower region of hydrogen pressures we used, then this would mean that an increase in pressure above 50 atm would lead to a decrease in adsorption and, consequently, in the cyclohexane isomerization rate. The reaction rate would then depend on the change in total pressure, and replacement of hydrogen by a nitrogen-hydrogen mixture at a constant total pressure would not have an appreciable effect on the cyclohexane isomerization rate. However, our experiments showed that the replacement of hydrogen by a nitrogen-hydrogen mixture at a constant total pressure substantially affected the rate of cyclohexane isomerization and consequently the role of hydrogen in the reaction studied cannot be reduced to the creation of hydrostatic pressure.

We carried out four series of experiments on the isomerization of cyclohexane at 340° under a pressure of hydrogen and a nitrogen-hydrogen mixture containing 50 ± 3% H_2 (see table). The arbitrary contact time *, input rate, and partial cyclohexane pressure remained approximately constant in each series of experiments. In these experiments we used a fresh portion of WS_2 catalyst (140 g, 59 ml), which was first kept for two days in a stream of hydrogen at 300°. The catalyst grain size was 3-5 mm. Since the hydrogen used contained up to 1% O_2, the apparatus described previously [1] was modified somewhat. Before entering the reactor, the compressed gas was passed through a tube with freshly reduced granulated copper (170 g) at 320° and then through a bomb with granulated potassium hydroxide (300g) and silica gel (300g).

An examination of the data in the table shows that the degree of isomerization of cyclohexane remained practically constant when the total pressure was increased by a factor of 2 while p_{H_2} = const. The slight decrease (about 2%) in the degree of reaction with a change from hydrogen to a nitrogen-hydrogen mixture at p_{H_2} = const was apparently caused by somewhat greater removal of the reaction products: the catalyzate yield was 79-86% in experiments with a nitrogen-hydrogen mixture, depending on the degree of dilution, and in experiments with hydrogen it was 86-91%. At the same time, replacement of nitrogen by hydrogen at a constant total pressure led to a sharp decrease in cyclohexane conversion. Thus, the decrease in the rate of heterogeneous catalytic isomerization of cyclohexane with an increase in hydrogen pressure, which we observed, could not be caused by the effect of hydrostatic pressure on the adsorption equilibrium of cyclohexane.

Adsorption of hydrogen and nitrogen on WS_2 under pressure. As has already been noted above, a reason for the observed effect of hydrogen pressure could be a decrease in the adsorption of cyclohexane as a result of covering of the catalyst surface by adsorbed gas. In this case one would expect that the retarding effect of an increase in pressure of any gas in the isomerization of cyclohexane would be determined by an increase in the adsorption of this gas on WS_2 over the given pressure range. In the previous section it was shown that the retarding effect of nitrogen pressure, if this effect exists at all, is extremely small. On the basis of the considerations presented above, one would expect that with an increase in pressure, the adsorption of nitrogen on WS_2 would increase much more slowly than the adsorption of hydrogen. In order to check this hypothesis, we investigated the adsorption of hydrogen and nitrogen on WS_2 at 300 and 400° and pressures up to 100 atm by the method of Frolich and White [5].

The adsorption apparatus (Fig. 1) consisted of a bomb 1 (250 cc in volume), an adsorber 2 (80cc in volume) and 400-atm 3 and 100-atm 4 standard gauges. For determination of the amount of gas passing into the adsorber, the volume of the bomb 1 was first determined with hydrogen and nitrogen. For this purpose the gas pressure in the bomb 1 was successively reduced by a definite number of scale divisions on gauge 3 through the gas meter 12 (connected to valve 6 instead of adsorber 2 during the calibration). The calibration was repeated several times and then the mean value of the gas volume corresponding to each scale division of gauge 3 was determined. The deviations of separate measurements from the mean values did not exceed 5%. The bomb 1 was placed in a thermostat 8, in which the temperature was maintained at 20 ± 0.2° during the experiments and calibration.

The adsorber was placed in an electric furnace 9; the temperature of the adsorber was controlled with two thermocouples, one of which 10 was placed in the body of the adsorber and the other 11, in the electric furnace. Particular attention was paid to the thermostatting of the adsorber. The leads from the electric furnace were carefully insulated with asbestos fiber and the adsorber was kept at the required temperature for 3-4 hr before the beginning of an experiment. The temperature fall along the inner wall of the adsorber did not exceed 3°. The adsorber was charged with 180 g of WS_2 catalyst (grain size 3-5 mm) heated for 20 hr in a stream of H_2 at 300°. Before an experiment, the catalyst in the adsorber was kept under vacuum (5 mm Hg) at the temperature of the adsorption determination for from 30 min to 4 hr and a change in the evacuation time within the given limits did not have an appreciable effect on the amount of gas adsorbed. Valve 7 was then closed and gas fed in separate portions (0.5-1.5 liter) from bomb 1 into the adsorber through valve 6. Each new portion of gas was fed into the adsorber when the reading of gauge 4 had not changed for 12 min. These operations were repeated until the pressure in the adsorber p_1 reached 97 atm. The volume of gas V_1 fed into the adsorber from the beginning of the experiment was calculated from the calibration of bomb 1.

* See [1] for calculation of arbitrary contact time.

TABLE

Isomerization of Cyclohexane at 340° under a Pressure of Hydrogen and a Nitrogen-Hydrogen Mixture

Expt. No.	Total pressure in atm	Partial pressure in atm			Rate in mole/hr			τ in sec	Dilution $(H_2+N_2):C_6H_{12}$	Catalyzate composition in weight %				$\frac{b}{a+b}\cdot 100$
		C_6H_{12}	H_2	N_2	C_6H_{12}	H_2	N_2			C_6H_{12}	$C_6H_5CH_3$ a	C_6H_{14} b	a + b	
38	50	2,63	47,4	—	0,0390	1,78	—	112	18,0	67,1	32,6	0,3	32,9	0,9
36	100	2,60	46,3	51,1	0,0341	1,68	1,85	117	37,5	67,1	32,5	0,4	32,9	1,2
33	100	2,72	51,6	45,7	0,0373	1,84	1,64	118	35,8	68,5	31,2	0,3	31,5	1,0
35	100	2,66	97,3	—	0,0376	3,57	—	115	36,6	72,7	26,9	0,4	27,3	1,5
37	100	2,62	97,4	—	0,0365	3,58	—	115	37,1	74,8	24,9	0,3	25,2	1,2
44	100	4,94	95,1	—	0,116	2,23	—	180	19,2	77,4	22,4	0,2	22,6	0,9
47	100	4,78	95,2	—	0,113	2,25	—	179	19,9	77,5	22,3	0,2	22,5	0,9
49	100	4,88	95,1	—	0,114	2,22	—	181	19,5	79,6	20,2	0,2	20,4	1,0
46	200	5,29	95,4	99,3	0,121	2,18	2,27	185	36,8	79,4	20,4	0,2	20,6	1,0
48	200	5,09	97,5	97,5	0,115	2,20	2,20	187	38,3	81,4	18,5	0,1	18,6	0,5
50	200	4,77	95,5	99,8	0,108	2,16	2,26	187	40,9	79,3	20,5	0,2	20,7	1,0
52	200	5,18	195	—	0,116	4,36	—	189	37,6	85,9	14,0	0,1	14,1	0,7
53	200	5,00	195	—	0,112	4,37	—	189	39,0	85,3	14,5	0,2	14,7	1,4
54	100	9,54	90,5	—	0,116	1,10	—	347	9,48	74,6	24,8	0,6	25,4	2,4
56	200	9,48	93,0	97,6	0,111	1,09	1,14	361	20,1	76,9	22,9	0,2	23,1	0,9
58	200	9,17	191	—	0,107	2,23	—	361	20,8	82,8	16,9	0,3	17,2	1,7
55*	100	9,63	90,4	—	0,114	1,07	—	357	9,39	78,5	21,1	0,3	21,5	1,4
57*	200	9,20	90,6	100	0,109	1,07	1,19	357	20,7	79,4	20,4	0,2	20,6	1,0
59*	200	9,71	190	—	0,113	2,21	—	364	19,6	84,4	15,4	0,2	15,6	1,3

* Experiments 55, 57, and 59 were carried out without preliminary regeneration of the catalyst in a stream of hydrogen.

To calculate the amount of adsorbed gas, it was necessary to determine the "free volume" of the adsorber. For this purpose the catalyst was replaced by an equal volume of copper rod. The catalyst volume was taken as equal to 24.0 cc (the density of WS_2 equals 7.5 g/cc *). Determination of the volume of the copper rod both by direct measurement of its dimensions and by calculation from the density of copper (8.92) lead to the same result. Experiments with the copper rod were carried out in the same way as with the catalyst.

The volume of adsorbed gas was determined graphically. For this purpose we plotted curves of V_1 against p_1 and V_2 against p_2, where V_2 is the volume of gas introduced into the adsorber with copper from the beginning of the experiment until the pressure p_2 was reached in the adsorber. From the graph we determined the differences $\Delta V = V_1 - V_2$ at different values of $p_1 = p_2$, corresponding to the volumes of adsorbed gas. We estimated the error in the volume measurements as ± 0.05 liter. The gas was not desorbed completely from the catalyst surface with the procedure used and therefore the amount of adsorbed gas was not determined accurately. However, the investigation carried out was suitable for the problem given above, i.e., to compare the change in the adsorption of nitrogen and hydrogen with an increase in their pressure.

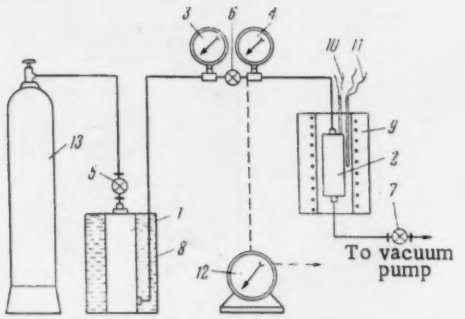

Fig. 1. Plan of apparatus for measuring adsorption under pressure.

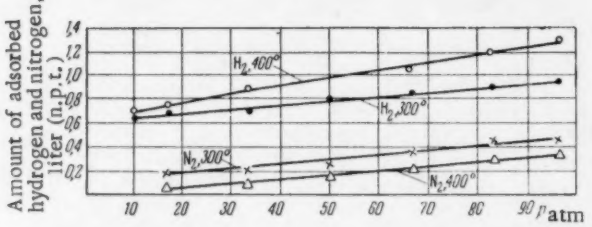

Fig. 2. Adsorption of hydrogen and nitrogen on WS_2.

The results of measuring the adsorption of nitrogen at 300 and 400° are given in Fig. 2. The data obtained show that the adsorption of nitrogen on WS_2 decreased somewhat with an increase in temperature and increased with a rise in pressure by approximately 0.2 liter over the pressure range 50-100 atm. We carried out analogous experiments with hydrogen. However, it was found that the catalyst surface was freed from adsorbed hydrogen more fully under a pressure of nitrogen than with evacuation to 5 mm. Thus, after the hydrogen had been pumped from the catalyst at 5 mm and the catalyst had been kept under 100 atm of nitrogen for several hours at the experimental temperature (400°) and again pumped out, the amount of adsorbed hydrogen (x_{H_2}) at 50 atm was 1.0 liter, while when the catalyst was only kept in vacuum, the amount was 0.75 liter. Figure 2 gives the results of measuring the adsorption of hydrogen at 300 and 400° with the catalyst first kept under a pressure of nitrogen. As these results show, the adsorption of hydrogen increased with an increase in pressure from 50 to 100 atm by 0.15 liter at 300° and by 0.3 liter at 400°. The curves obtained for the adsorption of hydrogen on WS_2 over the pressure range 10-100 atm is described satisfactorily by the following empirical equation:

$$x_{H_2} = \beta + \alpha p_{H_2}^{0.5}. \quad (1)$$

* We also determined the catalyst density pycnometrically (by displacement of benzene and n-hexane) and found it to equal 7.0 g/cc. The low value of the density was evidently caused by the incomplete displacement of air by liquid from the catalyst pores. Calculation of the catalyst volume for a density of 7.0 g/cc gave a value of 25.8 cc, i.e., a decrease in the "free volume" in the adsorber of 3.2%. Thus, with a catalyst density of 7.0 g/cc we would have obtained a somewhat higher volume of adsorbed gas than that determined (see below).

The data obtained make it possible for us to draw the qualitative conclusion that the increase in the adsorption of hydrogen with an increase in pressure does not differ substantially from the increase in the adsorption of nitrogen. Therefore, it seems improbable to us that the retardation of cyclohexane isomerization with an increase in hydrogen pressure is caused by a decrease in the adsorption of cyclohexane on the catalyst surface as a result of increase in the adsorption of hydrogen . Apparently, this problem can be solved conclusively only by investigation of the adsorption of cyclohexane itself under a pressure of hydrogen and nitrogen as there is the possibility that cyclohexane displaces adsorbed nitrogen from the catalyst surface, but is unable to displace chemisorbed hydrogen.

DISCUSSION OF EXPERIMENTAL RESULTS

The results presented above lead us to the hypothesis that hydrogen may have a specific role in the reaction studied. Below we attempt to give an explanation of the observed rules on the basis of existing ideas on the ionic mechanism of hydrocarbon isomerization. In studying the isomerization of cyclohexane to methylcyclopentane in the presence of anhydrous aluminum chloride, which they discovered, in 1932 Zelinskii and Turova-Polyak expressed the opinion [6] that this process proceeds through the intermediate dehydrogenation of cyclohexane with the liberation of hydrogen. Obolentsev [7] then applied this hypothesis to the isomerization of alkanes. It was subsequently shown [8, 9] that a pressure of hydrogen strongly retards the isomerization of n-hexane and cyclohexane in the presence of anhydrous aluminum chloride. On this basis, the hypothesis was put forward [9] that the isomerization includes an intermediate reversible stage involving the liberation of hydrogen and the equilibrium of this intermediate reaction determines the rate of the whole process. Finally, Nenitescu [10] was able to detect the liberation of small amounts of hydrogen during the isomerization of cyclohexane, methylcyclopentane, and methylcyclohexane when they were boiled with anhydrous $AlCl_3$.

In recent years, many investigations have been published on the isomerization of hydrocarbons over heterogeneous metal oxide catalysts, which have both isomerizing and hydrogenating-dehydrogenating activity. In studying the isomerization of n-hexane in the presence of a nickel aluminosilicate catalyst at 320-410°, Ciapetta and Hunter [11] established that this process is retarded as the partial hydrogen pressure increases over the range from 7.1 to 48.5 atm. On the basis of these data, Ciapetta [12] put forward the hypothesis that under the heterogeneous catalysis conditions he studied, the first stage of the isomerization of alkanes and cycloalkanes is their dehydrogenation. The olefins or "potential olefins" formed are then converted into carbonium ions capable of isomerization. Analogous conclusions were drawn by Mills et al. [13] and also Weisz and Swegler [14], who used various methods to investigate the mechanism of hydrocarbon isomerization in the presence of heterogeneous, bifunctional catalysts. We should note that the sulfides of some metals and, in particular, tungsten sulfide [15], are also bifunctional catalysts. Moreover, it is known that hardly any isomerization of alkanes occurs over heterogeneous bifunctional catalysts in the absence of hydrogen (for example, under a pressure of nitrogen) [11, 16]. The role of hydrogen here cannot be limited to suppression of polymerization and hence maintenance of the high activity of the catalyst. The formation of carbonium ions capable of isomerization apparently requires the presence of water (or hydroxyl groups) on the surface of oxide catalysts and hydrogen sulfide (or SH groups) on the surface of sulfide catalysts. It may be assumed that the formation of these groups occurs not only during the preparation of the catalyst, but also during its operation as a result of reaction with hydrogen .

On the basis of the facts and considerations presented, it may be assumed that the isomerization of cyclohexane we investigated proceeds through the three following main stages with the dehydrogenation and hydrogenation stages reaching equilibrium:

$$C_6H_{12} \rightleftarrows C_6H_{10}+H_2 \quad (a)$$

$$C_6H_{10} \rightarrow C_5H_7CH_3 \quad (b)$$

$$C_5H_7CH_3+H_2 \rightleftarrows C_5H_9CH_3 \quad (c)$$

The over-all rate of the reaction is then determined by the equilibrium concentration of cyclohexene in stage (a) and the rate of the slowest stage (b), which proceeds by an ionic mechanism. In this case the hydrogen pressure may have a double effect on the cyclohexane isomerization rate: 1) the hydrogen pressure retards the isomerization, displacing the equilibrium of stage (a) toward the starting material (cyclohexane) and 2) the hydrogen pressure promotes the isomerization of cyclohexane by creating active centers for the realization of the ionic mechanism of stage (b).

The equilibrium partial pressure of cyclohexene, which, from the point of view presented, is one of the factors controlling the over-all reaction rate, is determined by the equation:

$$p_{C_6H_{10}} = \frac{K p_{C_6H_{12}}}{p_{H_2}}, \tag{2}$$

where K is the equilibrium constant. The second controlling factor is the rate of stage (b), which may be described by the equation:

$$w = k \cdot p^{0.5}_{C_6H_{10}} = \frac{k \cdot K^{0.5} \cdot p^{0.5}_{C_6H_{12}}}{p^{0.5}_{H_2}}, \tag{3}$$

where $\underline{w}$ and $\underline{k}$ are the rate and rate constant of stage (b), respectively. Here we assumed that the order of stage (b) with respect to cyclohexene and, consequently, with respect to cyclohexane, equals 0.5.* It is known that the rate equations of most heterogeneous catalytic reactions studied include the partial pressures of the starting materials and the reaction products to the power $n \approx 0.5$ [17]. According to Temkin [18], these fractional powers reflect the relation between the kinetic and the adsorption characteristics of the different sites of the heterogeneous surface of the catalyst.

The relation of the reaction rate to the partial hydrogen pressure following from equation (3) does not agree with our experimental data, according to which the order of the reaction with respect to cyclohexane n = 0.5:

$$w = \left(a + \frac{b}{p^{0.5}_{H_2}}\right) p^{0.5}_{C_6H_{12}} \tag{4}$$

(see equation (3) in [2]). From a comparison of (3) and (4) it follows that in actual fact the isomerization of cyclohexane is retarded by an increase in the partial hydrogen pressure to a lesser extent than follows from equation (3). If our hypothesis on the existence of an equilibrium dehydrogenation stage (see above) is correct then we must conclude that there are also factors as a result of which an increase in the hydrogen pressure facilitates the isomerization of cyclohexane. As has already been mentioned above, such a factor could be the activation of the catalyst by hydrogen . On the basis of this hypothesis, we may introduce into equation (3) a new factor characterizing the relation of the reaction rate to the amount of adsorbed hydrogen (x_{H_2}). In particular, for this purpose we may use the approximate relation (1) which we found for the adsorption of hydrogen on WS_2 at 300° and 400°.

By combining (3) and (1), we obtain:

$$w = kKf \left(\frac{p_{C_6H_{12}}}{p_{H_2}}\right)^{0.5} (\beta + \alpha p^{0.5}_{H_2}), \tag{5}$$

where $\underline{f}$ is the proportionality coefficient, or

$$w = kKf \left(\alpha + \frac{\beta}{p^{0.5}_{H_2}}\right) p^{0.5}_{C_6H_{12}}. \tag{6}$$

It is readily seen that equation (6) is completely identical with the empirical equation (4).

From equations (4) and (6) it follows:

$$a : b = \alpha : \beta. \tag{7}$$

Unfortunately, our data on the adsorption of hydrogen is insufficiently accurate and, due to the incompleteness of desorption before the beginning of measurements, give a low value for β. Therefore, the check of the

*According to our experimental data [1], the order of the reaction with respect to cyclohexane equals 0.4 so that satisfactory agreement with experiment is given by calculations with n = 0.5.

accuracy of relation (7) is only of a qualitative nature. According to our adsorption measurements, the ratio $\alpha:\beta$ is 0.1 at 300° and 0.2 at 400°. On the other hand, according to our kinetic data (Table 4 in [2]), the ratio a : b equals 0.02 at 320°-340° and 0.06 at 370-380°. These two ratios (α : b and a : b) are similar in order of magnitude and increase with an increase in temperature. Thus, our experimental data are in qualitative agreement with the hypotheses underlining the derivation of equation (6).

Laboratory assistant E. A. Udal'tsova and mechanic Yu. I. Ryzhov assisted with the work.

SUMMARY

1. The rate of isomerization of cyclohexane to methylcyclopentane on an industrial WS_2 catalyst under a pressure of a nitrogen-hydrogen mixture (1 : 1) is practically independent of the partial nitrogen pressure.

2. The adsorption of nitrogen and hydrogen on WS_2 at 300 and 400° over the pressure range up to 100 atm was investigated.

3. Possible reasons for the retardation of cyclohexane isomerization on WS_2 with an increase in the partial hydrogen pressure were analyzed.

4. From the hypothesis that there is an equilibrium dehydrogenation stage in cyclohexane isomerization and activation of the catalyst by adsorbed hydrogen we derived an approximate equation, which agrees qualitatively with the experimental data obtained on the effect of hydrogen pressure on the rate of the process studied.

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CORROSION AND ELECTROCHEMICAL BEHAVIOR OF STAINLESS STEELS UNDER CATHODE POLARIZATION IN NITRIC ACID SOLUTIONS

COMMUNICATION 2. CATHODE PROCESSES ON STAINLESS STEELS IN NITRIC ACID SOLUTIONS

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We previously [1,2] demonstrated the possibility of destroying the passive state and examined the characteristics of dissolution of stainless steels under cathode polarization in nitric acid solutions. The potentials at which dissolution of steels is observed are determined by the kinetics of the cathode process on the electrodes. In this connection it is interesting to examine the nature of the cathode processes on stainless steels for determining the mechanism of the dissolution of stainless steel under the given conditions. In published work on the kinetics of electrode processes on stainless steels in nitric acid solutions, the cathode processes have been examined without the consideration of the possibility of the destruction of the passive state of the steels by cathode polarization [3] and also without consideration of the properties of nitric acid [4].

For understanding the nature of cathode reactions of stainless steels there is definite interest in the examination of cathode processes in nitric acid solutions on an inert (platinum) electrode, which have recently been studied in a number of works. The most detailed description of the processes occurring during cathode polarization of a platinum electrode in nitric acid solutions was given in [5]. In this work it was shown that on a platinum cathode in nitric acid there are two possible, mutally exclusive, processes: the liberation of hydrogen and the reduction of nitric acid to nitrous acid, which is autocatalyzed by nitrous acid. In dilute acid solutions, (below 3.4 N), only liberation of hydrogen was observed, while in more concentrated solutions, the cathode liberation of hydrogen is preceded by the higher potential process of cathode reduction of nitric acid to nitrous acid. We would note that dilute solutions (< 20%) of nitric acid are completely dissociated, while more concentrated solutions contain homeopolar molecules of nitric acid [6,7]. The cathode reduction of nitric acid to nitrous acid may also occur in dilute solutions if nitrous acid is added to them. The limiting current of nitric acid reduction increases with an increase in the concentration of nitric and nitrous acids and the temperature, and in the presence of a platinized platinum electrode (instead of a smooth platinum electrode) and decreases with an increase in the solution stirring rate.

The mechanism of cathode reduction of nitric acid was examined in [4,8,9]. In [9] it was shown that the stage limiting the rate of the cathode reduction of nitric acid, which is represented by the equation $3H^+ + NO_3^- + 2e^- \rightarrow HNO_2 + H_2O$, is the electrode reaction $NO_2 + e^- + H^+ \rightarrow HNO_2$. The limiting current of nitric acid reduction is determined by the rate of the heterogeneous chemical reaction $HNO_2 + HNO_3 \rightleftharpoons 2NO_2 + H_2O$, which forms the consumable potential-determining particles (depolarizer) of NO_2. However, these ideas on the mechanism of nitric acid reduction do not allow for its degree of dissociation in solution. This gap was filled in [10-12], in which, in our opinion, it was correctly pointed out that the oxidizing cathode depolarizer is undissociated homeopolar molecules of nitric acid. However, the ideas of the author on the mechanism of the autocatalytic action of nitrous acid were not founded on experiment.

EXPERIMENTAL

The date obtained [2] on the dissolution of stainless steels under cathode polarization and the cathode polarization curves (Fig. 1) make it possible to examine the characteristics of cathode processes on stainless steels in nitric acid solutions. From a knowledge of the activation potentials, which we determined from the experimental relations of the corrosion rate to the potential, it is possible to divide the cathode processes on stainless steels into the active and passive states.

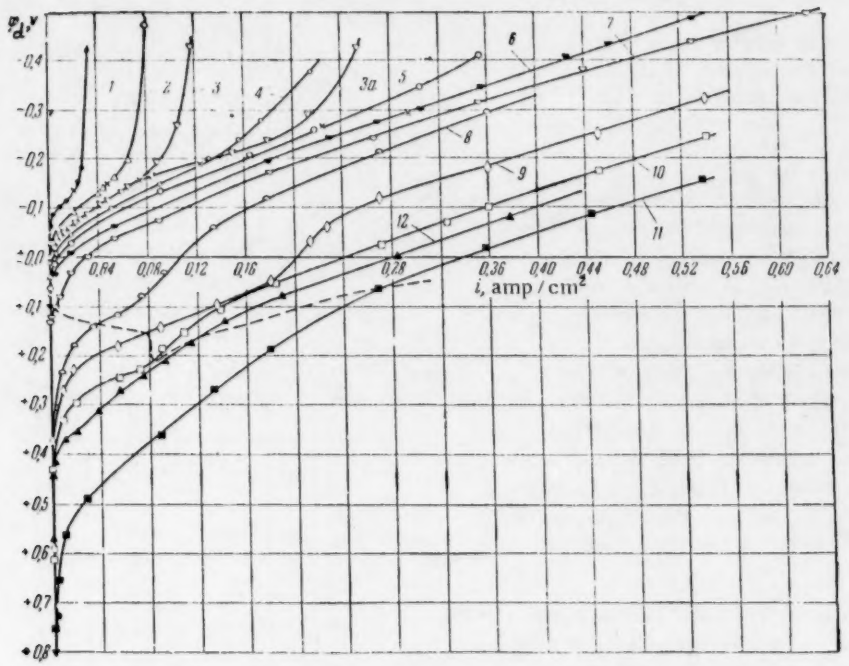

Fig. 1. Cathode polarization curves for the steel 1Kh18N11B in nitric acid solutions at 20° : 1) 1%; 2)2%; 3) 3%; 3a) 3% with stirring at 2500 rev/ min; 4) 5%; 5)8%; 6) 12%; 7) 20%; 8) 29%; 9) 35%; 10) 40%; 11) 50%; 12) 55%.

In Fig. 1, a broken line is drawn through the points on the cathode curves corresponding to the activation potentials of the steel in solutions of various concentrations. The sections of the cathode curves below the broken line refer to the passive state of the steel, while those above the broken line refer to activated steel. From Fig.1 it follows that on the cathode polarization curves for 20% HNO_3 and more concentrated solutions, i.e., solutions with homeopolar molecules, there are sections referring both to the passive and the active states of the steels. In more dilute (below 20%) solutions, which are completely dissociated, the cathode curves refer to the active state of the steel.

Let us first examine cathode processes on steels in completely dissociated nitric acid solutions. An examination of the cathode polarization curves for stainless steels in dilute, completely dissociated nitric acid solutions, reveals the following characteristics of the cathode process: a) the overvoltage of the cathode process on stainless steels cannot be less than that on smooth platinum; this follows from Fig. 2 for 3% HNO_3; b) the cathode process may proceed at an appreciable rate only on activated stainless steel in contrast to concentrated solutions in which the cathode process proceeds at an appreciable rate on a passive surface also; c) cathode polarization curves at the potential of the active state ($\varphi_{a.s.}$) snow inflection points (the points of the cathode polarization curves corresponding to $\varphi_{a.s.}$ are denoted by crosses in Fig. 1), which indicates a change at $\varphi_{a.s.}$ from control of the cathode process by its overvoltage to control of rate of supply of the depolarizer; d) diffusion threshold of the cathode reaction (cathode current density at $\varphi_{a.s.}$) depends linearly on the acid concentration and the steel dissolution rate, which follows from the relations presented in Figs. 3 and 4, which we established.

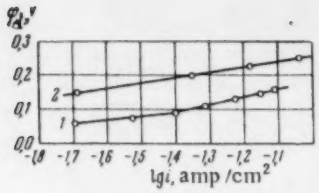

Fig. 2. Cathode polarization curves for the steel 1Kh18N11B and platinum in 3% nitric acid at 20°: 1) steel, v = 0.22; 2) Pt, v = 0.15.

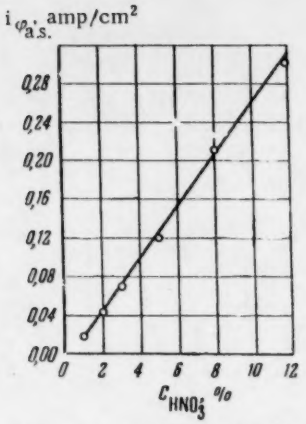

Fig. 3. Relation of the diffusion threshold of the cathode process on the stainless steel 1Kh18N11B to the nitric acid concentration.

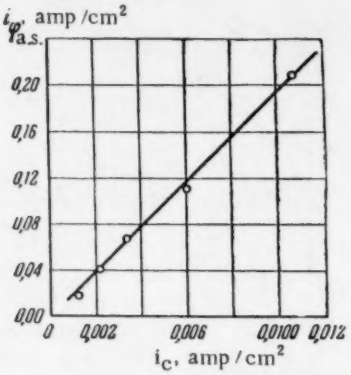

Fig. 4. Relation of the cathode current density on the steel 1Kh18N11B to the rate of its dissolution in nitrous acid solutions at the potential of the active state.

We should also note that stirring the acid, which did not affect the overvoltage of the cathode process, led to an increase in the diffusion cathode threshhold (cf. curves 3 and 3a in Fig. 1). In the plotting of polarization curves in relatively negative potential regions (below $\varphi_{a.s.}$) there was a strong negative increase in the electrode potentials and the beginning of vigorous gas evolution. This was considered in detail in the previous communication [2]. In the light of the characteristics of the cathode process on stainless steels we observed and available literature data on cathode processes on a platinum electrode in nitric acid solutions, it is possible to examine the nature of the cathode process on activated stainless steels.

The fact that there is a lower overvoltage on steels than on platinum, on which the overvoltage of cathode processes is usually minimal [12], leads to the conclusion that the cathode process on stainless steels in completely dissociated nitric acid solutions is different than that on platinum, i.e., is not hydrogen liberation. In dilute nitric acid solutions, the cathode process on stainless steels proceeds at appreciable rates beginning with the activation potential (see Fig. 1). From this we may draw the conclusion that active sections of the surface catalyzed the cathode process on stainless steels. The presence of these sections on the steel surface indicates active solution and therefore it is more accurate to consider that the corrosion products catalyzed the cathode process on activated steels. The cathode process on activated stainless steels suffers diffusion retardation at the potential of the active state (an inflection point on the cathode polarization curves is observed at $\varphi_{a.s.}$), i.e., from the moment of the decrease in corrosion rate. Therefore, it may be considered that the rate of supply of corrosion products affects the rate of the cathode process or, in other words, the corrosion products participate in the cathode process as an autocatalyst.

In the first approximation, the mechanism of the autocatalytic action of the corrosion products on the cathode process on activated stainless steels may be understood if it is considered that during the solution from the active state elements present in the stainless steel, for example, iron and chromium, pass into solution as divalent ions [13], but they are determined analytically in nitric acid solutions mainly as trivalent ions, due to their oxidation in the solution. The oxidation of these ions may proceed by the reaction $2Me^{2+} + NO_3^- + 3H^+ \rightarrow 2Me^{3+} + HNO_2 + H_2O$ with the reduction of the nitrate ions to nitrous acid. Nitrate ions may be be reduced to nitrous acid by means of oxidation-reduction systems of the elements present in the stainless steels: Fe^{3+}/Fe^{2+}, Cr^{3+}/Cr^{2+}, and Ti^{4+}/Ti^{3+}, the normal potentials of which are less than that of the system NO_3^-/HNO_2 [14]. The possibility of the reduction of nitric acid to nitrous acid by ferrous ions has also been demonstrated experimentally [15].

If the corrosion products or more accurately some cations present in them may reduce nitrate ions to nitrous acid, which is an autocatalyst of nitric acid reduction [5, 8, 9], then on activated steels there is essentially cathode reduction of nitric acid, analogous to the process on a platinum cathode in dilute nitric acid solutions with nitrous acid added. Nitrous acid actually participates in the cathode process on activated stainless steels. Thus, the addition to 3% nitric acid of 10 g per liter of urea, which destroys HNO_2 [16], increases the overvoltage of the cathode reaction on the steel 1Kh18N11B by 0.015 v when I = 0.01 amp/cm^2 and decreases the diffusion threshold of the cathode process. Consequently, it may be considered that the cathode process on activated stainless steels in completely dissociated nitric acid solutions is the reduction of nitrate ions to nitrous acid, which is autocatalyzed by nitrous acid formed by the reaction of the corrosion products, mainly Fe^{2+} and Cr^{2+}, with nitrate ions and hydrogen.

In the general form, the cathode reduction of nitrate ions on activated stainless steels may be represented schematically by a series of equations:

$$2\cdot(2Me^{2+}+NO_3^{'}+3H^+ \rightarrow HNO_2+2Me^{3+}+H_2O), \quad (1)$$

$$HNO_2+H^++NO_3^{'} \rightarrow 2NO_2+H_2O, \quad (2)$$

$$2\cdot(NO_2+H^++e^- \rightarrow HNO_2). \quad (3)$$

In the presence of excess HNO_2, formed by reactions (1) and (3) and consumed by reaction (2), with a steady rate of the cathode process, the nitrous acid may be decomposed according to the equation:

$$3HNO_2 \rightarrow HNO_3+2NO+H_2O. \quad (4)$$

The over-all equation of the cathode process on activated stainless steels is then represented in the form:

$$2Me^{2+}+NO_3^{'}+4H^++e^- \rightarrow 2Me^{3+}+NO+2H_2O. \quad (5)$$

Calculation shows that the normal potential of reaction (5) for the cathode process on active iron equals + 1.35 v; in the case of active chromium, the normal potential is even more positive. It should be mentioned that it is only in the first approximation that equation (5) describes the cathode process on active metals like iron and its alloys in completely dissociated nitric acid solutions. The stages of the cathode reduction of nitrate ions to nitrous acid on an active steel electrode expressed by equations (1) - (4) reflect its essential nature and difference from the analogous cathode process on an inert platinum electrode. A necessary condition for the reduction of nitrate ions to nitrous acid both on steel and on platinum cathodes is the participation of nitrous acid as an autocatalyst. While the reduction of nitrate ions to nitrous acid on a platinum cathode in completely dissociated nitric acid solutions may occur only when nitrous acid is added, in the case of a steel cathode, its dissolution guarantees the formation of nitrous acid due to the reaction of the corrosion products (Fe^{2+}, Cr^{2+}) with nitrate ions and hydrogen.

The absence of an effect of stirring the solution on the overvoltage of the process indicates that the stage limiting the rate of the cathode reduction of nitrate ions to HNO_2 on steels, as on platinum, is the electrode reaction (2). The diffusion threshold of the cathode reduction of nitrate ions to nitrous acid in nitric acid solution of a given concentration on platinum and activated stainless steel cathodes is determined by the nitrous acid concentration in the layer of solution immediately adjacent to the electrode, i.e., in the diffusion layer. The HNO_2 concentration limits the rate of the heterogeneous reaction (2), which forms the cathode depolarizer NO_2. In the case of a stainless steel cathode in completely dissociated nitric acid solutions, the HNO_2 concentration in the diffusion layer is determined largely by the rate of reaction (1), which in its turn, depends on the composition of the stainless cathode and its dissolution rate. Therefore, stirring the acid, which leads to an increase in the dissolution rate of the steel cathode [2], and, consequently, in the absolute concentration of ions of the type Fe^{2+} and Cr^{2+} in the corrosion products, increases the diffusion threshold since the rate of formation of nitrous acid by reaction (1) on a steel cathode is evidently greater than the rate of its removal from the electrode due to stirring of the solution. In the case of an inert platinum cathode, stirring the acid leads solely to the removal of nitrous acid and, consequently, to a decrease in the limiting cathode current.

A characteristic of the cathode reduction of nitric acid to nitrous acid is the fact that this process and the cathode liberation of hydrogen compete, as has been demonstrated for a platinum cathode [5]. The previously noted [2] disruption of the reproducibility of anode and cathode polarization curves on stainless steels in nitric acid solutions at potentials more negative than φ_H and the effects observed thereupon are evidently due to the appearance of the competition of these two cathode processes, i.e., the reduction of nitric acid, the progress of

which is determined by the accumulation of nitrous acid, and the discharge of hydrogen ions, whose occurrence at appreciable rates involves the liberation of hydrogen bubbles, which remove the nitrous acid from the electrode surface. The observed positive increase in the potential of steels with time at a constant external cathode current density is due to the accumulation of nitrous acid, which is known [5] to decrease the polarization of cathodes in the system HNO_3/HNO_2.

Let us examine the cathode processes on stainless steels in nitric acid solutions with concentrations above 20%. The presence of homeopolar molecules in these solutions imposes certain characteristics on the course of the cathode polarization curves. From a comparison of the cathode polarization curves for platinum [5] and passive stainless steel in nitric acid solutions (see Fig. 1) it follows that the overvoltage of the cathode process on platinum is less than on passive steel. Thus, in 40% HNO_3 at $i = 0.01$ amp/cm^2, the potential of platinum equals + 1.01 v, while that of passive steel 1Kh18N11B equals + 0.33 v. The higher overvoltage of the cathode process on passive stainless steel in comparison with platinum must be due to the difference in the properties of the surfaces of platinum and steel. Obviously, together with the reduction of homeopolar nitric acid molecules to nitrous acid, on passive stainless steels there is reduction of Me^{3+} ions to Me^{2+} ions, which by reacting with nitric acid according to equation (1), further increase the HNO_2 concentration in the diffusion layer. Me^{3+} ions are present at the steel surface due to its solution from the passive state [13]. As a result of this, the limiting current of nitric acid reduction on stainless steel should be greater than on platinum. In actual fact, in 29% nitric acid on platinum, the limiting current density equals 0.01 amp/cm^2 [17] and is a factor of 4 less than that on passive steel 1Kh18N11B at the activation potential (see Fig. 2, curve 8) although the rate of the cathode process at φ_a is not the limiting value. The cathode curves were plotted under natural convection conditions at 20° in both cases.

In nitric acid solutions containing homeopolar molecules, there is cathode reduction of the phase passivating film at the activation potentials, as in more dilute solutions. The different nature of the pH dependence of the activation potential $\varphi_a = -0.46 - 1.07$ pH, to that in completely dissociated solutions $\varphi_a = 0.026 - 0.095$ pH indicates that there is a difference in the course of the reduction of the passivating film on stainless steels in the presence and in the absence of homeopolar nitric acid molecules.

The presence of homeopolar molecules in nitric acid solutions has a characteristic effect on the sections of the cathode polarization curves referring to the active state of the steel. Figure 1 shows that on curves 7, 8, 9, and 10 in the region of potentials more negative than φ_a there are limiting diffusion currents, whose magnitude changes in relation to the nitric acid concentration and passes through a maximum. It is not possible to consider the reasons for the appearance of this limiting current and the effect of the nitric acid concentration on it at present on the basis of available experimental material. The presence of the limiting current here is evidently connected with a change in the state of the surface, i.e., with the beginning of solution of steel from the active state.

The nature of the cathode processes on activated stainless steels is the same in nitric acid solutions containing homeopolar molecules and in completely dissociated nitric acid solutions. On activated steels there is cathode reduction of nitric acid to nitrous acid, which is autocatalyzed by nitrous acid. When homeopolar nitric acid molecules are present in solution, nitrous acid is formed both due to reduction of the homeopolar molecules and due to the reaction of nitrate ions and hydrogen with the corrosion products according to equation (1).

SUMMARY

On stainless steels in nitric acid solutions there is cathode reduction of nitric acid to nitrous acid, which is autocatalyzed by nitrous acid. The nitrous acid is formed in completely dissociated solutions by the reaction of nitrate ions and hydrogen with the corrosion products (Fe^{2+} and Cr^{2+}), while in solutions containing homeopolar nitric acid molecules, it is also formed due to reduction of the latter. Cathode liberation of hydrogen on active steels is observed in the region of more negative potentials.

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CORROSION AND ELECTROCHEMICAL BEHAVIOR OF STAINLESS STEELS UNDER CATHODE POLARIZATION IN NITRIC ACID SOLUTIONS

COMMUNICATION 3. EFFECT OF STEEL COMPOSITION

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The composition of stainless steels has a substantial effect on their corrosion behavior in aggressive media. The corrosion and electrochemical behavior of stainless steels in relation to their composition has been studied by various methods [1-6]. However, the mechanism of the effect of alloying elements on the corrosion resistance of stainless steels in nitric acid media, in which they are widely used as construction materials, has not been elucidated at all up to now.

EXPERIMENTAL

In the present work we present the preliminary results of an investigation of the effect of the composition of stainless steels on their corrosion and electrochemical behavior in nitric acid solution under conditions where the passive state is destroyed. The compositions of the steels studied are given in Table 1. The steels were investigated in a tempered state. For each material we determined the relation of the corrosion rate to the potential and the cathode polarization curves [7] in 3% HNO_3 at 20°. We should note that from the relation of corrosion rate to potential it is possible to determine the anode polarizability in the active state (tan β), the activation potential (φ_a), and the potential of the active state ($\varphi_{a.s.}$), which clearly define the corrosion behavior of steels when their passive state is destroyed.

Parameters (tan β, φ_a, and $\varphi_{a.s.}$) characterize, respectively, the ease of ionization of the alloy in the active state, the lower limit of stability of the passive state, and the beginning of passivating adsorption on the steel [7]. We should also note that the potentials at which dissolution of stainless steels in nitric acid solutions is observed are determined by the kinetics of the cathode reduction of nitric acid to nitrous acid, which is autocatalyzed by nitrous acid. The nitrous acid in 3% nitric acid, which is completely dissociated, may be formed due to reduction of nitrate ions by dissolution products of steel, for example, Fe^{2+} and Cr^{2+} ions [8].

Behavior of alloys of the iron–chromium system. An examination of the corrosion and electrochemical behavior of iron alloys containing various amounts of chromium is of particular interest. Chromium is the main alloying element, the presence of ~ 14% of which makes iron–chromium alloys stainless. The iron–chromium alloys we had differed not only in the chromium content, but also in the carbon content. Therefore, in assessing the effect of chromium, we started from the content of it in the solid solution, i.e., that not bound in carbides. The chromium content of the alloy was converted into the chromium content of the solid solution in the same way as in [9].

Figure 1 gives relations of corrosion rate to potential, which are, in essence, anode curves, and Fig 2 gives cathode polarization curves for the alloys studied and also iron and chromium. The relation of corrosion rate to potential for chromium, which is corrosion-resistant at all the potentials studied, merges with the ordinate axis

TABLE 1

Chemical Composition of Materials Investigated

Grade	Composition in %							Other elements	Chromium content of solid solution in weight %
	C	P	S	Mn	Si	Cr	Ni		
1Kh13	0,09	0,024	0,017	0,40	0,31	12,77	0,21	—	11,8
1Kh17	0,11	—	—	0,61	0,65	16,33	0,41	—	15,7
1Kh28	0,08	—	—	0,40	0,25	26,83	0,35	—	26,2
2Kh13	0,20	0,025	0,023	0,33	0,34	12,70	0,29	—	10,5
Kh313	0,31	0,027	0,012	0,29	0,28	12,67	0,25	—	9,2
1Kh17N2	0,14	0,018	0,012	0,41	0,32	17,1	2,0	—	—
1Kh18N9	0,07	0,03	0,019	1,28	0,44	17,33	9,2	—	—
1Kh18N9T	0,09	0,037	0,011	0,91	0,68	16,63	10,97	0,87 Ti	—
1Kh18N11B	—	0,024	0,011	1,05	0,64	18,05	11,85	1,05 Nb	—
1Kh18N12MZT	0,075	0,025	0,008	1,01	0,62	16,28	13,73	3,74 Mo 0,34 Ti	
Alloys of the chromium–iron system	0,040	0,025	0,02	traces	—	1,80	—	—	1,75
	0,035	0,02	0,02	traces	0,011	3,72	—	—	3,67
	0,030	0,015	0,015	traces	—	5,72	—	—	5,7
	0,025	0,02	0,01	—	0,015	6,76	—	—	6,75
	0,015	0,02	0,02	—	—	14,0	—	—	13,85
Iron	Spectrally pure								
Chromium	Electrolytic								

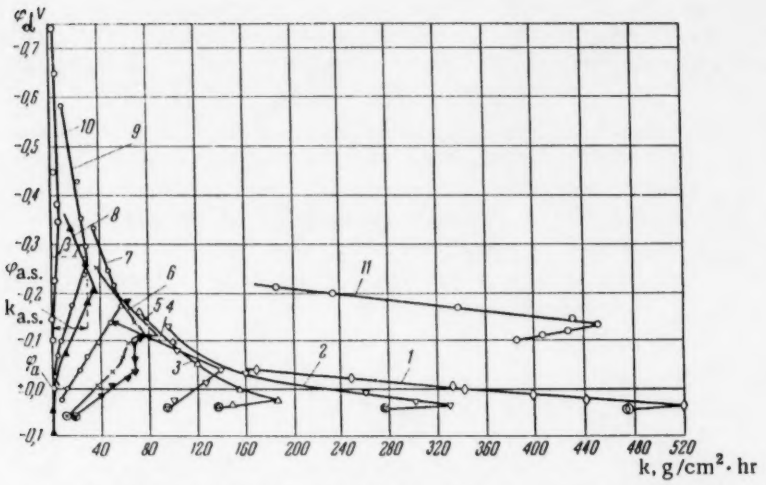

Fig. 1. Potential dependence of the corrosion rate of iron alloys with various chromium contents in 3% nitric acid at 20° 1)1.75%; 2)3.67%; 3)5.7%; 4)6.75%; 5)9.2%; 6)10.5%; 7)11.8%; 8)13.85%; 9)15.7%; 10)26.2%; 11) iron.

in Fig. 1. Figure 3 gives values obtained from the anode and cathode polarization curves for the activation potential (φ_a), the potential of the active state ($\varphi_{a.s}$), the anode polarizability (tan β) and the maximum corrosion rate of the alloys ($k_{a.s.}$) in the active state, the fraction of active surface at the standard potential (α), and also the overvoltage of the cathode process (η) in relation to the chromium content of the solid solution.

From Figs. 1 and 2 it follows that even minimal additions of chromium had a specific effect on the corrosion and electrochemical behavior of alloys in nitric acid. Alloying of iron with even 1.75% of chromium led to a displacement of the anode and cathode polarization curves by more than 100 mv toward positive potentials. Thereupon, the potential of the alloy increased with time. On the other hand, in the case of pure iron, the potential fell with time.

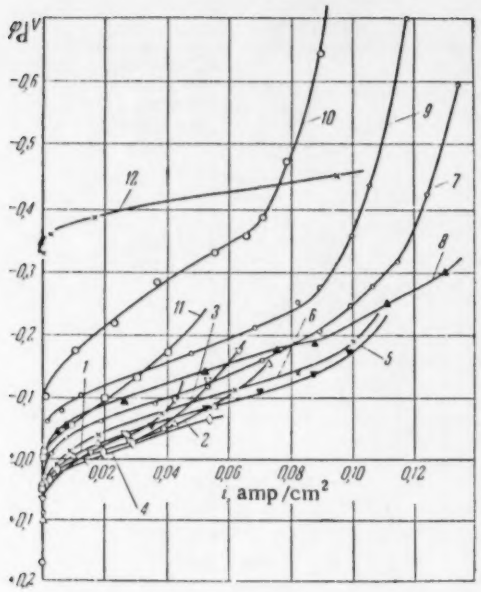

Fig. 2. Cathode polarization curves in 3% nitric acid at 20° for iron-chromium alloys with various chromium contents: 1)1.75%; 2)3.67%; 3)5.7%; 4)6.75%; 5)9.2%; 6)10.5%; 7)11.8%; 8)13.85%; 9)15.7%; 10)26.2%; 11)iron; 12) chromium.

The fall in the potential of iron in 3% nitric acid with time is due to the possibility of cathode liberation of hydrogen in this solution in addition to the reduction of nitrate ions to HNO_2. A fall in potential with time is characteristic of the solution of iron with the liberation of hydrogen [10]. When 1.75% of chromium was introduced into iron, the fall in potential with time was no longer observed as the displacement in potential toward positive values occurring thereupon evidently made the liberation of hydrogen thermodynamically impossible.

The relations of the corrosion rate to potential are the same for alloys containing less than and more than 14% of chromium; they all can be activated completely and protected cathodically; only alloys containing more than 14% of chromium are passive at the stationary potential, while those with less than this amount are partially passivated. The fraction of active surface is less, the higher the chromium content of the alloy (curve of α in Fig. 3). By the stationary potential we mean the mean value of the potential of the alloy during the experiment in the absence of cathode polarization. Figure 3 shows that an increase in the chromium content of the solid solution led to a displacement of activation potential (φ_a) toward negative values, as occurs in sulfuric acid solutions [2]. The potentials of the active state ($\varphi_{a.s.}$) of alloys with up to 6% of chromium hardly changed, while above 6%, they became more negative. With an increase in the chromium content of the solid solution, the anode polarizability (tan β) increased, while the maximum solution rate in the active state ($k_{a.s.}$) decreased. By the maximum corrosion rate in the active state, we mean the corrosion rate at the potential of the active state. The relations of the maximum corrosion rate and the anode polarizability to the chromium content have an exponential nature. The maximum solution rate from the active state of alloys with a chromium content up to approximately 7% may be represented in the form: $\log k_{a.s.} = 3 - 0.167c$, and with a chromium content above 7%, by $\log k_{a.s.} = 2.67 - 0.069c$, where c is the chromium content of the solid solution in atomic percent.

Thus, the characteristics of the potential dependence of the dissolution rate for alloys with various chromium contents makes it possible to establish the mechanism of the alloying of iron by chromium. The role of chromium in Fe–Cr alloys is reduced to widening the potential range in which the alloys are passive (φ_a is displaced toward negative values), facilitating the passivation of alloys (decreasing the fraction of active surface and the potential of the active state), and also hampering the solution of alloy from the active state (tan β increases). The increase in the chromium content of the alloys leads to gradual increase in corrosion resistance of the alloys in the active state. As was expected, no stability limits were observed for iron-chromium solid solutions during their solution from the active state. The existence of these limits in iron-chromium alloys [9, 11] is connected with self-passivation of definite planes of the crystal lattice [12]. Self-passivation was excluded in our experiments (by cathode polarization).

In contrast to suluric acid solutions, in nitric acid solutions a change in the chromium content of the alloys had a considerable effect on the kinetics of the cathode process (Fig. 2). An examination of the cathode polarization curves shows that the alloying of iron with chromium first decreases the overvoltage of the cathode process (η), from 2 to 6% of chromium the latter hardly changes, and then above 6% of chromium, it increases (Fig. 3). Considering the kinetics of the cathode process, the decrease in the rate of dissolution of iron-chromium alloys in nitric acid solution with an increase in their chromium content (Fig. 1) must be explained by a combination of the effects of chromium both in retarding the solution from the active state and facilitating passivation of the

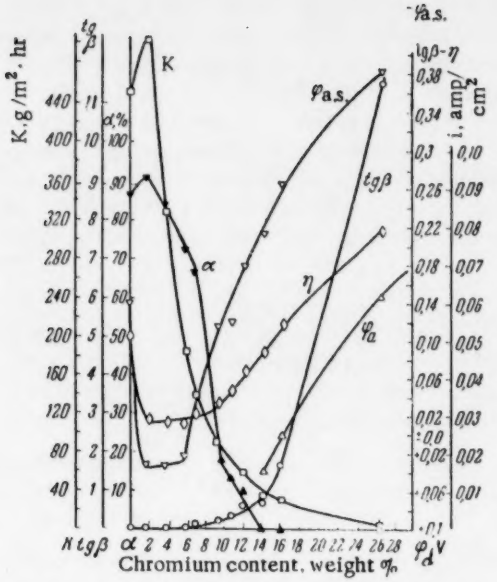

Fig. 3. Effect of chromium content of the iron-chromium solid solution on the activation potential (φ_a), the potential of the active state ($\varphi_{a.s.}$) the fraction of active surface (α) at the stationary potential, the anode polarizability (tan β), the maximum corrosion rate ($k_{a.s.}$) in the active state, and the overvoltage of the cathode process (η) at i = 0.02 a/cm² in 3% nitric acid at 20°.

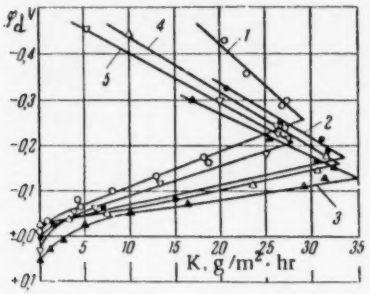

Fig. 4. Potential dependence of the rate of corrosion of stainless stels in 3% nitric acid: 1)1Kh17; 2) 1Kh17N2; 3) 1Kh18N9; 4) 1Kh18N9T; 5) 1Kh18N12MZT.

alloy and in increasing the overvoltage of the cathode process of nitric acid reduction.

The effect of the nickel content on the corrosion and electrochemical behavior of stainless steels in nitric acid solution may be examined on the example of the steels 1Kh17, 1Kh17N2, and 1Kh18N9, which hardly differ in their chromium content. Figures 4 and 5 show anode and cathode polarization curves for these steels and also for the steels 1Kh18N9T and 1Kh18N12MZT, while Table 2 gives the values of some parameters characterizing the corrosion and electrochemical behavior of metals and alloys when their passive state is destroyed. From Table 2 it follows that with an increase in the nickel content of the steels, there was an increase in the fraction of active surface (at a potential $\varphi = -0.1$ v); the activation potentials and the potential of the active state became more positive, the anode polarizability decreased, and the maximum corrosion rate of the steel in the active state increased. An increase in the nickel content reduced the overvoltage of the cathode process. The results presented show that the introduction of nickel into stainless steels has the opposite effect to chromium on their corrosion and electrochemical behavior in nitric acid solution under cathode polarization. Alloying of steels with nickel leads to contraction of the region of the stable passive state, hampering of their passivation, and facilitation of the solution of steels from the active state. As the steels contained approximately the same amount of chromium and differed little in the impurity content (Mn, Si, P, and S), the characteristics of alloying with nickel may be regarded as due to the replacement of iron atoms by nickel in the steel. By comparing the anode and cathode polarization curves for the steels 1Kh18N9, 1Kh18N9T, and 1Kh18N12MZT (curves 3, 4, and 5 in Figs. 4 and 5), it is possible to draw some conclusions on the role of titanium and molybdenum in the corrosion behavior of stainless steels in nitric acid solutions.

Alloying the steel 18h18N9 with titanium (curves 3 and 4 in Figs. 4 and 5) led to a change in the parameters in the same directions (Table 2) as when chromium was added. An exception was a slight decrease in the overvoltage of the cathode reaction when titanium was added.

A comparison of the behavior of steels 1Kh18N9T and 1Kh18N12MZT (Table 2) shows that alloying the steel with molybdenum, which suppressed the action of excess nickel, reduced the fraction of the active surface, displaced the potential of the active state toward negative values, increased the anode polarizability, decreased the corrosion rate in the active state, and increased the overvoltage of the cathode process. Consequently, it may be considered that the introduction of molybdenum into steel affects its corrosion and electrochemical behavior in nitric acid solution analogously to chromium.

In conclusion, let us consider the fact that the limiting cathode currents on stainless steels and alloys depend

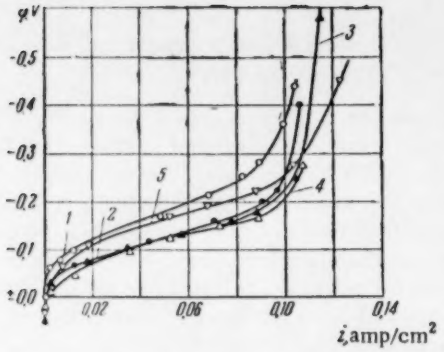

Fig. 5. Cathode polarization curves in 3% nitric acid at 20° for stainless steels: 1) 1Kh17; 2) 1Kh17N2; 3) 1Kh18N9; 4) 1Kh18N9T; 5) 1Kh18N12MZT.

on the composition of the latter (Figs. 2 and 5). This fact, which is paradoxical at first glance, may be explained by considering the nature of the cathode process [8]. The magnitude of the limiting cathode current of nitric acid reduction depends on the nitrous acid concentration in the diffusion layer. The concentration of HNO_2 in the diffusion layer is determined largely by the rate of reduction of nitrate ions to nitrous acid by the dissolution products of the alloy and, consequently, depends on the rate of dissolution of the alloy and the qualitative composition of the corrosion products.

SUMMARY

1. A study was made of the effect of the chromium and nickel content of stainless steels on their corrosion and electrochemical behavior in nitric acid solution when their passive state is destroyed.

2. The decrease in the dissolution rate of iron–chromium alloys with an increase in their chromium content is caused by the combined effect of chromium both in retarding solution from the active state and facilitating passivation of the alloy and in increasing the overvoltage of the cathode process of nitric acid reduction.

3. The introduction of nickel into stainless steels has the opposite effect to chromium on their corrosion and electrochemical behavior in nitric acid solution.

TABLE 2

Corrosion and Electrochemical Behavior of Stainless Steels in 3% Nitric Acid

Grade	Element content in %	α, %	tg β	φ_a, V	$\varphi_{a.s.}$, V	$k_{a.s.}$ in g/m². hr	φ in v at i_c=0.02 a/cm²
1Kh17	Ni = 0,41	31	0,020	+0,00	—0,26	29	—0,12
1Kh17N2	Ni = 2,0	54	0,0124	+0,005	—0,17	33,5	—0,08
1Kh18N9	Ni = 9,2	77	0,010	+0,05	—0,13	35	—0,08
1Kh18N9T	Ti = 0,87	59	0,0118	—0,020	—0,16	33	—0,07
1Kh18N12MZT	Ti = 0,34 Mo = 3,74	43	0,012	+0,035	—0,205	28	—0,11

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THEORY OF CHAIN – THERMAL FLAME PROPAGATION

COMMUNICATION 2. TWO ACTIVE CENTERS WITH DIFFERENT DIFFUSION COEFFICIENTS

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In a previous article [1], relations were obtained for determining the flame propagation rate in a system with two active centers with identical diffusion coefficients. This problem for two active centers with identical diffusion coefficients was solved by reducing it to the problem with a simplified chain reaction scheme and an active center of one type, examined in the first article [2], which was devoted to the theory of chain-thermal propagation of a laminar flame in a homogeneous gas mixture. In a number of papers we examined the relation of the flame propagation rate to pressure and temperature [3, 4, 1], the effect of the thermal conductivity of the fuel mixture and the diffusion coefficients of the active centers on the flame propagation rate [5, 4], and the role of branching and chain termination in the chain reactions with relatively low rates of the branching processes [4].

In the present article we derive relations which may be used to calculate the rate of flame propagation and the distribution of the concentration of active centers in relation to a change in temperature for an unbranched reaction scheme, including two forms of active center with different diffusion coefficients.

Reaction scheme and system of equations. We adopted the following form of reaction scheme in which A and B are the starting materials, C is the final reaction product, and P_1 and P_2 are the active centers:

$$M + A \to 2P_1 + M, \quad \Phi_1 = h_{R_1} R_1(T'); \tag{1}$$

$$M + B \to 2P_2 + M, \quad \Phi_2 = h_{R_2} R_2(T'); \tag{1'}$$

$$P_1 + B \to C + P_2, \quad Q_1 n_1 = h_1 F_1 n_1 = h_1 K_1(T')\, n_B n_1; \tag{2}$$

$$P_2 + A \to C + P_1, \quad Q_2 n_2 = h_2 F_2 n_2 = h_2 K_2(T')\, n_A n_2; \tag{3}$$

$$P_2 + C \to B + P_1, \quad Q_3 n_2 = h_3 F_3 n_2 = h_3 K_3(T')\, n_C n_2; \tag{2'}$$

$$P_1 + C \to A + P_2, \quad Q_4 n_1 = h_4 F_4 n_1 = h_4 K_4(T')\, n_C n_1; \tag{3'}$$

$$2P_1 + M \to A + M, \quad X_1 n_1^2 = h_{W_1} W_1(T')\, n_1^2; \tag{4}$$

$$2P_2 + M \to B + M, \quad X_2 n_2^2 = h_{W_2} W_2(T')\, n_2^2. \tag{4'}$$

The expressions for the rates of heat evolution (or absorption) are given on the right. Here h_i is the heat effect of the reaction in cal/mole, n_1 and n_2 are the concentrations of the active centers P_1 and P_2 in mole/g of mixture, n_A, n_B, and n_C are the concentrations of substances A, B, and C in mole/g of mixture, K_i and W_i are the reaction rate constants in $g^2/cc \cdot mole^2 \cdot sec$, R_i is the chain initiation rate in mole/cc · sec, and T' is the temperature in °K. It was assumed that the diffusion coefficients of the starting materials D_A and D_B and of the reaction product D_C equal the thermal conductivity coefficient ($\lambda = c\rho D_A = c\rho D_B = c\rho D_C$), and therefore the rates of chain initiation (1) and (1') and also the expression for F_i are written as functions of temperature alone.

The system of equations describing the satisfactory propagation of a laminar planar flame for the reaction scheme presented and the conditions adopted reduces to three equations:

$$\lambda p \frac{dp}{dT} - Bcp + Q_1 n_1 + Q_2 n_2 + Q_3 n_2 + Q_4 n_1 + \Sigma X_i n_i^2 + \Phi = 0, \tag{5}$$

$$D_1 \frac{d^2 n_1}{dx^2} - B \frac{dn_1}{dx} + F_2 n_2 + F_3 n_2 - F_1 n_1 - F_4 n_1 + R_1 - W_1 n_1^2 = 0, \tag{6}$$

$$D_2 \frac{d^2 n_2}{dx^2} - B \frac{dn_2}{dx} + F_1 n_1 + F_4 n_1 - F_2 n_2 - F_3 n_2 + R_2 - W_2 n_2^2 = 0, \tag{7}$$

where $B = u\rho$, $D_1 = \rho D_{P_1}$, $D_2 = \rho D_{P_2}$, $T = T' - T_0$, $\Phi = \Phi_1 + \Phi_2$, $\Sigma X_i n_i^2 = X_1 n_1^2 + X_2 n_2^2$ and $p = dT/dx$; $\underline{x}$ is the coordinate on the axis normal to the flame surface in cm, $\underline{u}$ is the flow rate along the axis $\underline{x}$ in cm/sec, ρ is the density in g/cc, λ is the thermal conductivity in cal/cm · sec · deg, $\underline{c}$ is the heat capacity at constant pressure in cal/g · deg, and D_{P_1} and D_{P_2} are the diffusion coefficients of the active centers P_1 and P_2 in cm^2/sec.

The index "0" refers to the initial state of the fresh mixture ($T' = T'_0$), the index "Г" to the state at the combustion temperature ($T' = T'_\Gamma$), and the index "m" to the state corresponding to the maximum value of the temperature gradient ($T' = T'_m$).

The sum of the functions of the heat evolution rates in (5) and the sums of the functions of the reaction rates in (6) and in (7) equal zero when $T' = T'_0$ and $T' = T'_\Gamma$. The limiting conditions for equations (5), (6), and (7) are:

$$T' = T'_0,\ n_1 = n_{10},\ n_2 = n_{20},\ \frac{dT}{dx} = \frac{dn_1}{dx} = \frac{dn_2}{dx} = 0; \tag{8}$$

$$T' = T'_\Gamma,\ n_1 = n_{1\Gamma},\ n_2 = n_{2\Gamma}\ \frac{dT}{dx} = \frac{dn_1}{dx} = \frac{dn_2}{dx} = 0. \tag{9}$$

Such conditions correspond to a flame without heat losses to the surrounding medium and were adopted in the previous examination [1, 2].

Determination of flame propagation rate. Allowance for the rates of quadratic chain termination, which considerably complicates the final results, does not lead to an appreciable change in the theoretical flame propagation rate [4]. Therefore, we will first assume that $W_1 = W_2 = 0$. We will subsequently show how to calculate the flame propagation rate with allowance for the rates of quadratic chain termination by using the approximate relations obtained in [4].

The method of solving the given problem, which is based on representing the solutions of equations of type (6) and (7) with the conditions (8) and (9) as polynomials of the second degree, was examined in detail and proved in [2]. According to [2] and on the basis of (5), (6), and (7), the concentrations of active centers at a temperature $T = T_m$, corresponding to the maximum value of the temperature gradient $p = p_m$, may be written in the following form:

$$n_{1m} = t_1 + (R_{1m} + G_{2m} n_{2m} - G_{1m} n_{1m} - B l_1 p_m) N_1, \tag{10}$$

$$n_{2m} = t_2 + (R_{2m} + G_{1m} n_{1m} - G_{2m} n_{2m} - B l_2 p_m) N_2, \tag{11}$$

where $l_1 = \dfrac{n_{1\Gamma} - n_{10}}{T_\Gamma}$, $\quad l_2 = \dfrac{n_{2\Gamma} - n_{20}}{T_\Gamma}$,

$$N_1 = \frac{r}{2D_{1m} p_m^2}, \quad N_2 = \frac{r}{2D_{2m} p_m^2},$$

$$t_1 = n_{10} + l_1 T_m, \quad t_2 = n_{20} + l_2 T_m,$$

$$r = T_m (T_r - T_m), \quad G_1 = F_1 + F_4,$$

$$G_2 = F_2 + F_3 \text{ and} T_m = 0{,}5T_r.$$

By solving (10) and (11) and rearranging, we find:

$$n_{1m} = \frac{t_1 + (R_{1m} - Bl_1 p_m) N_1 + [(t_1 N_2 + t_2 N_1) + (R_m - Blp_m) N_1 N_2] G_{2m}}{1 + G_{1m} N_1 + G_{2m} N_2}, \tag{12}$$

$$n_{2m} = \frac{t_2 + (R_{2m} - Bl_2 p_m) N_2 + [(t_1 N_2 + t_2 N_1) + (R_m - Blp_m) N_1 N_2] G_{1m}}{1 + G_{1m} N_1 + G_{2m} N_2}, \tag{13}$$

where $l = l_1 + l_2$ and $R = R_1 + R_2$.

By substituting (12) and (13) in (5) and considering that when $T = T_m$, $p = p_m$ and $(dp/dT)_m = 0$, and also by using the previously obtained relation $B = \eta p_* = \eta p_m$ [2], in which $\eta = 4\lambda_0/cT_m$, we obtain, by introducing the symbolism given with (10) and (11):

$$A_1 p_*^6 + A_2 p_*^4 + A_3 p_*^2 + A_4 = 0, \tag{14}$$

where $A_1 = 4c\eta D_{1m} D_{2m}$.

$$A_2 = 2c\eta r (G_{1m} D_{2m} + G_{2m} D_{1m}) + 2\eta r (S_{1m} l_1 D_{2m} + S_{2m} l_2 D_{1m}) -$$

$$- 4D_{1m} D_{2m} (S_{1m} t_1 + S_{2m} t_2) - 4D_{1m} D_{2m} \Phi_m,$$

$$A_3 = \eta l (S_{1m} G_{2m} + S_{2m} G_{1m}) r^2 - 2r (t_1 D_{1m} + t_2 D_{2m}) (S_{1m} G_{2m} + S_{2m} G_{1m}) -$$

$$- 2r\Phi_m (G_{1m} D_{2m} + G_{2m} D_{1m}) - 2r (S_{1m} R_{1m} D_{2m} + S_{2m} R_{2m} D_{1m}),$$

$$A_4 = - R_m r^2 (S_{1m} G_{2m} + S_{2m} G_{1m}),$$

$$S_1 = Q_1 + Q_4 = h_1 F_1 + h_4 F_4,$$

$$S_2 = Q_2 + Q_3 = h_2 F_2 + h_3 F_3.$$

Allowance for the chain initiation rates does not have a substantial effect on the theoretical value of the flame propagation rate with the exception of special cases when the fuel mixture contains substances which decompose readily to form active centers. Therefore, by neglecting the rates of chain initiation, i.e., by assuming that $R_1 = R_2 = R = \Phi = 0$, from (14) we obtain

$$A_1 p_*^4 + A_2' p_*^2 + A_3' = 0, \tag{15}$$

where A_2' and A_3' are A_2 and A_3 when $R_1 = R_2 = \Phi = 0$.

The flame propagation rate will be determined by the relation which is found from the relation $B = \eta p_*$ with allowance for the symbols given with (5), (6), and (7):

$$u_0 = \frac{1}{\rho_0} \eta p_*, \tag{16}$$

where p_* is determined from equation (14) or from the approximate equation (15).

For determining the flame propagation rate, from relation (16) and equation (15) it is possible to obtain a simpler approximate relation, similar to those which were derived in previous work [1, 2, 5]. With the approximate assumption that $A_1 \approx 0$ in (15) and also considering that $A_2' \approx 2c\eta r (G_{1m} D_{2m} + G_{2m} D_{1m})$, we find

$$p_*^2 = \frac{(t_1 D_{1m} + t_2 D_{2m})(S_{1m} G_{2m} + S_{2m} G_{1m})}{c\eta (G_{1m} D_{2m} + G_{2m} D_{1m})} \left(1 - \frac{2q}{\varkappa}\right), \tag{17}$$

where $\frac{2q}{\varkappa} = \frac{2q_1 q_2 (t_1 + t_2)}{(t_1 \varkappa_1 q_1 + t_2 \varkappa_2 q_2)}$,

$$\varkappa_1 = \frac{cD_{10}}{\lambda_0}, \qquad \varkappa_2 = \frac{cD_{20}}{\lambda_0}, \qquad D_{10} = D_{1m} q_1,$$

$$D_{20} = D_{2m} q_2, \quad q_1 = \frac{\mu_0}{\mu_m} \left(\frac{T_0'}{T_m'}\right)^{a_1 - 1}$$

when $D_{P_1} \sim (T')^{a_1}$, $q_2 = \frac{\mu_0}{\mu_m} \left(\frac{T_0'}{T_m'}\right)^{a_2 - 1}$

when $D_{P_2} \sim (T')^{a_2}$, $\eta = 4 D_m q \frac{1}{\varkappa T_m}$

and $D_m = \frac{t_1 D_{1m} + t_2 D_{2m}}{t_1 + t_2}$.

By substituting p_* from (17) in (16) and considering the symbols given with (10) and (11), we obtain an approximate relation for determining the flame propagation rate

$$u_0 = \varphi \varphi_D \frac{1}{\rho_0} \sqrt{\frac{(n_{1r} D_{1m} + n_{2r} D_{2m})(S_{1m} G_{2m} + S_{2m} G_{1m})}{2cT_r (G_{1m} + G_{2m})}}, \tag{18}$$

where

$$\varphi = 2 \sqrt{\frac{2q}{\varkappa} \left(1 - \frac{2q}{\varkappa}\right)}, \tag{19}$$

$$\varphi_D = \sqrt{\frac{(n_{1r} D_{1m} + n_{2r} D_{2m})(G_{1m} + G_{2m})}{(n_{1r} + n_{2r})(G_{1m} D_{2m} + G_{2m} D_{1m})}}. \tag{20}$$

Relation (18) may be presented in a form coinciding with that of the relations obtained in previous work [1, 2, 5] for simpler cases if we introduce the effective total concentration of an active center of one type n_Γ, the effective diffusion coefficient D_{Pm}, and the effective value Q_m. After simple rearrangements, from (18) and (20) we obtain

$$u_0 = \varphi \frac{1}{\rho_0} \sqrt{\frac{n_r Q_m \rho_m D_{Pm}}{2cT_r}}, \tag{21}$$

where

$$n_r = (n_{1r} + n_{2r}) \frac{(n_{1r} D_{1m} + n_{2r} D_{2m})}{(n_{1r} + n_{2r})} \frac{(G_{1m} + G_{2m})}{(G_{1m} D_{2m} + G_{2m} D_{1m})} \tag{22}$$

$$D_{Pm} = \frac{n_{1r} D_{P1m} + n_{2r} D_{P2m}}{n_{1r} + n_{2r}}, \tag{23}$$

$$Q_m = \frac{S_{1m} G_{2m} + S_{2m} G_{1m}}{G_{1m} + G_{2m}}. \tag{24}$$

Previously, in the examination of flame decomposition [2], the mechanism of the successive (unbranched) chain reaction was represented by a simplified scheme with an active center of one type. The simplified scheme was introduced to facilitate the solution of the problem of flame propagation in a system reacting by a chain mechanism. Relations (21)-(24) confirm the reality of the simplified chain reaction scheme adopted previously [2, 4] and make it possible to determine for this simplified scheme the effective concentration of an active center of one type at the combustion temperature (22), the effective diffusion coefficient (23), and the effective rate

constant of the chain propagation process, which equals $2Q_m/cT_\Gamma$ according to (24). All these effective values are determined from data for the reaction scheme with two active centers and different diffusion coefficients.

Relations (18) and (21) do not allow for the rates of chain initiation and quadratic termination. By using the approximate relations which were obtained in [4] and also presented in [1], we find from (21) the final relation for determining the flame propagation rate u_0 with allowance for all the processes(1), (1'), (2), (3), (2'), (3'), (4) and (4'):

$$u_0 = \varphi\xi\psi \frac{1}{\rho_0} \sqrt{\frac{n_\Gamma Q_m \rho_m D_{pm}}{2cT_\Gamma}}, \tag{25}$$

where n_Γ, D_{pm}, and Q_m are found from relations (22), (23), and (24), while the rate coefficients ξ and ψ which respectively allow for the effect of the rates of chain initiation and quadratic termination, are calculated from the relations:

$$\xi = \sqrt{\frac{1}{2}\left(1 + \sqrt{1 + \frac{16q\varkappa cT_\Gamma R_m}{(\varkappa - 2q)^2 n_\Gamma^2 Q_m}}\right)}, \tag{26}$$

$$\psi = \left(1 + \frac{qcT_\Gamma W_m}{\varkappa Q_m}\right)^{-\frac{1}{2}}, \tag{27}$$

where $R_m \approx R_{1m} + R_{2m}$ and $W_m \approx W_{1m} + W_{2m}$, while $q/\varkappa$ is found from the corresponding relation given with (17). This representation of the over-all effective rates of chain initiation and termination in the form of the sums of the rates for different active centers with different diffusion coefficients is not completely strict in comparison with the case of equal diffusion coefficients [1]. However, when ξ and ψ differ little from unity, relations (26) and (27) may be used successfully and this is usually so in actual cases.

Assuming, as was done in [2], that the distribution of the concentrations of active centers P_1 and P_2 is determined by the values at $T = T_m$ (this assumption was shown to be permissible in [2]),in accordance with (12) and (13) and with allowance for the symbols given with (10) and (11) we obtain the temperature dependence of the concentration of active centers:

$$n_1(T) = \frac{(4D_{1m}D_{2m}p_m^4 l_1)T + [G_{2m}A_n + 2D_{2m}p_m^2(R_{1m} - \eta l_1 p_m^2)]T(T_\Gamma - T)}{4D_{1m}D_{2m}p_m^4 + 2p_m^2(G_{1m}D_{2m} + G_{2m}D_{1m})T(T_\Gamma - T)}, \tag{28}$$

$$n_2(T) = \frac{(4D_{1m}D_{2m}p_m^4 l_2)T + [G_{1m}A_n + 2D_{1m}p_m^2(R_{2m} - \eta l_2 p_m^2)]T(T_\Gamma - T)}{4D_{1m}D_{2m}p_m^4 + 2p_m^2(G_{1m}D_{2m} + G_{2m}D_{1m})T(T_\Gamma - T)}, \tag{29}$$

where $A_n = 2p_m^2(l_1D_{1m} + l_2D_{2m})T + (R_m - \eta l p_m^2)T(T_\Gamma - T)$, and $p_m = p_*$ is found from the solution of (14) or (15) or from the approximate relation (17).

In contrast to the relations $n_1(T)$ and $n_2(T)$ obtained in [2] for the case when the diffusion coefficients of the two active centers are equal, the relations (28) and (29) are derived with allowance for the rates of chain initiation.

DISCUSSION OF RESULTS OBTAINED

Let us examine some of the consequences of relation (21) or (25). By assuming for simplicity that $F_{3m} = 0$ and $F_{4m} = 0$ in (24), we obtain for Q_m the simpler relation $Q_m = (h_1 + h_2)F_{1m}F_{2m}/(F_{1m} + F_{2m})$. The value of Q_m, on which depends the rate of heat evolution in (25) and, consequently, the flame propagation rate, is determined, as in [1], by the least of the values F_{1m} or F_{2m}. When $F_{1m} = F_{2m}$, the value $Q_m = (h_1 + h_2)F_{1m}/2 = (h_1 + h_2)F_{2m}/2$. The value of Q_m is independent of $n_{1\Gamma}$ and $n_{2\Gamma}$ and of the separate heat effects, but is determined by the algebraic sum of the heat effects of the successive processes of chain propagation. The heat evolution rate also depends on the product $n_\Gamma D$ [relations (22) and (23)], the value of which will be determined mainly by the one of the

products $n_{1\Gamma}D_{P1m}$ or $n_{2\Gamma}D_{P2m}$ which is greatest under the given conditions. The active center with the greatest product $n_{i\Gamma}P_{im}$ will be the determining (driving) active center. For the case examined in [1] with equal diffusion coefficients, the driving active center will be that with the greatest concentration at the combustion temperature.

The product of the two fractions in the right-hand part of relation (22), i.e., the value $n_\Gamma/(n_{1\Gamma} + n_{2\Gamma})$, will always lie between the two possible limiting values D_{1m}/D_{2m} and D_{2m}/D_{1m}. Let us examine yet another product $n_\Gamma D_{Pm}$ obtained from relations (22) and (23), when $F_{3m} = F_{4m} = 0$ (this means that F_{1m} will appear in relation (22) instead of G_{1m}, and F_{2m} instead of G_{2m}). This product is obviously determined to a considerable extent by the diffusion current of active centers or the driving active center which has the greatest product $n_{i\Gamma}D_{Pim}$. However, the diffusion current of the driving active center also depends on the ratio of the rates of the successive processes (2) and (3), i.e., on the ratio of the values F_{1m} and F_{2m} as the diffusion current depends not only on $n_{1\Gamma}$ and $n_{2\Gamma}$, but also on the concentration of the driving active center at $T = T_m$, which depends, in its turn, on the rate of consumption and formation of the driving active center. Let us assume, for example, that $n_{1\Gamma}D_{1m} > n_{2\Gamma}D_{2m}$, then the value of n_Γ from relation (22) will depend substantially on the magnitudes of $F_{1m}D_{2m}$ and $E_{2m}D_{1m}$. If $F_{1m}D_{2m} > F_{2m}D_{1m}$, then the concentration of P_1 at $T = T_m$ will depend strongly on the rate of consumption of P_1 by process (2). This is explained by the high rate of consumption of P_1. If $F_{1m}D_{2m} < F_{2m}D_{1m}$, then the concentration of P_1 in the reaction zone will depend to a lesser extent on the diffusion current as the rate of formation of P_1 by process (3) is comparatively large. However, as follows from an examination of the product $n_\Gamma D_{Pm}$, on the whole, the flame propagation rate in a system with an unbranched chain reaction is determined to a greater extent by the diffusion flow of active centers, which is obviously completely physical. In cases where there is a strongly branched reaction or an unbranched reaction with a high rate of generation of active centers (this may occur when the fuel mixture contains small amounts of ozone or some other substance which decomposes rapidly with the formation of active centers at temperatures below the combustion temperature), the leading role of the diffusion of active centers in flame propagation will be excluded due to the high rate of active center formation in the reaction zone as a result of chain branching or initiation.

The driving active center will mainly determine the nature of the relations of flame propagation rate to combustion pressure and temperature. The concentrations of the different active centers may depend differently on the combustion pressure and temperature for a mixture of a given initial composition [1, 3, 5]. The rate of change of the concentration of a given active center with pressure and temperature, changes with a change in the initial composition of the mixture [3]. Therefore, with a decrease in pressure, the driving role may pass from one active center to another and will depend on the mixture composition. Therefore, the effective activation energy, determined from formulas that do not allow for the diffusion of active centers, will depend on the initial composition of the fuel mixture [1, 3].

Relation (25) makes it possible to determine the true constants and activation energies of the elementary processes from the experimental relations of the flame propagation rate to combustion pressure and temperature [1]. Relations (16) and (14) make it possible to determine the experimental values of the constants and activation energies with high accuracy.

Numerical calculations. The relations obtained make it possible to calculate the absolute theoretical values of the flame propagation rates for actual cases by using the values of the rate constants and activation energies of the elementary processes found experimentally (by purely kinetic methods independent of flames) and required for the calculation. The scheme presented at the beginning of the article is found in the combustion of halogen-hydrogen mixtures. As an example we chose chlorine-hydrogen fuel mixtures, whose kinetics have been studied thoroughly and are represented by the following chain reaction scheme:

$$Cl+H_2 \rightarrow HCl+H, \quad h_1 = -2\cdot 10^3, \quad K_1 = 10^{13,9}\rho^2 \exp\left(-\frac{5500}{RT'}\right);$$

$$H+Cl_2 \rightarrow HCl+Cl, \quad h_2 = 4{,}6\cdot 10^4, \quad K_2 = K_2'\rho^2 \exp\left(-\frac{2500}{RT'}\right);$$

$$H+HCl \rightarrow H_2+Cl, \quad h_3 = 2\cdot 10^3, \quad K_3 = 10^{13,4}\rho^2 \exp\left(-\frac{5200}{RT'}\right);$$

where the two values $K_2' = 10^{13.7}$ and $K_2' = 10^{13.4}$ were adopted for the preexponent K_2'. The relations presented for the reaction rate constants were taken from the data of Trotman-Dickenson [6] and Schumacher [7].

The data for two mixtures obtained by thermodynamic calculations are given in Table 1, where μ is the molecular weight of the mixture.

The diffusion coefficients of the active centers and the thermal conductivity for the two mixtures were taken from the work of Hellwig and Anderson [8]: $D_{P10} = 0.19$ (Cl at.) and $D_{P20} = 1.04$ (H at.) when $a_1 = a_2 = 1.9$ and $\lambda_0 = 8.6 \cdot 10^{-5}$.

The results of calculations from relation (25) are given in Table 2, which also gives experimental data for corresponding mixtures obtained by Bartolome [9]. Due to some uncertainty about the value of the pre-exponent of process (3), the calculations were carried out with the two values of K_2' given above. In both cases $\xi = 1.00$ and $\psi = 1.00$, although the extremely high value $K_{R_1} = 10^{16} \rho^2 \exp(-57{,}000/RT')$ was adopted for the rate constant of chlorine atom generation. For the rate constant of quadratic chain termination we adopted the value $2 \cdot 10^{-32}$ $cc^2/molecules^2 \cdot sec$. The results of the calculations show that allowance for the rate of quadratic chain termination has hardly any effect on the calculated value of the flame propagation rate (as $\psi = 1.00$).

TABLE 1

Thermodynamic Calculation Data

Value	T'	n_B (H_2)	n_A (Cl_2)	n_C (HCl)	n_1 (Cl)	n_2 (H)	μ	c
Dimensions	°K	mole/g of mixture					g/mole	cal/g·deg
0,5 H_2 + +0,5 Cl_2	$T_0' = 293$	$1{,}37 \cdot 10^{-2}$	$1{,}37 \cdot 10^{-2}$	0	0	0	36,5	0,208
	$T_m' = 1389$	$7{,}36 \cdot 10^{-3}$	$6{,}85 \cdot 10^{-3}$	$1{,}26 \cdot 10^{-2}$	—	—	35,8	0,225
	$T_r' = 2485$	$1{,}01 \cdot 10^{-3}$	$1{,}65 \cdot 10^{-5}$	$2{,}51 \cdot 10^{-2}$	$2{,}25 \cdot 10^{-3}$	$1{,}26 \cdot 10^{-4}$	35,1	0,241
0,6 H_2 + +0,4 Cl_2	$T_0' = 293$	$2{,}03 \cdot 10^{-2}$	$1{,}35 \cdot 10^{-2}$	0	0	0	29,6	0,258
	$T_m' = 1337$	$1{,}36 \cdot 10^{-2}$	$6{,}75 \cdot 10^{-3}$	$1{,}32 \cdot 10^{-2}$	—	—	29,5	0,275
	$T_r' = 2380$	$6{,}97 \cdot 10^{-}$	$1{,}67 \cdot 10^{-6}$	$2{,}64 \cdot 10^{-2}$	$6{,}08 \cdot 10^{-4}$	$2{,}23 \cdot 10^{-4}$	29,3	0,293

A comparison of the experimental values of the flame propagation rate with the theoretical values calculated from relation (25) and presented in Table 2 indicates that they agree satisfactorily. In the first article [2], where a study was made of flame propagation in a system with a simplified chain reaction scheme, including an active center of one type, the results of theoretical calculation according to a relation of type (25) were compared with results obtained by numerical integration of the original system of equations. The difference in the numerical values of the flame propagation rates in these cases was a few percents. Considering this fact and also data on the comparison of the experimental and theoretical values given in Table 2, we may conclude that the theoretical examination for systems with an unbranched chain reaction accurately describes the actual flame propagation process.

The results obtained (Table 2) demonstrate the possibility of determining the true constants and activation energies of the chain propagation processes from the experimental relations of the flame propagation rate to combustion temperature.

The author is very grateful to V. N. Kondrat'ev for valuable advice and help with the work.

TABLE 2

Experimental and Theoretical Values of the Flame Propagation Rates (cm/sec) for Chlorine-Hydrogen Mixtures

Mixture composition	$0.6H_2 + 0.4Cl_2$	$0.5H_2 + 0.5Cl_2$
Experimental data of Bartolome [9]	405	350
From relation (25) with $K_2' = 10^{13.7}$	347	368
From relation (25) with $K_2' = 10^{13.4}$	252	278

SUMMARY

1. For an unbranched chain reaction with two active centers we obtained relations for determining the flame propagation rate with allowance for diffusion of the two active centers with different diffusion coefficents and also with allowance for the rates of chain initiation and quadratic termination.

2. The flame propagation rates were calculated for two cases of the combustion of chlorine-hydrogen mixtures and these agreed satisfactorily with experimental data.

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SYNTHESIS OF ORGANIC COMPOUNDS OF PHOSPHORUS BY REACTION BETWEEN PHOSPHORIC ANHYDRIDE AND ALUMINUM PHENOXIDES

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In the search for new macromolecular compounds, particularly compounds stable to the action of high temperatures, some organic phosphorus-containing macromolecular compounds have been prepared. Organic derivatives of polyphosphorus acids are comparatively readily hydrolyzed with water [1, 2], and they have therefore not found practical application as synthetic materials. Burg and co-workers [3] obtained many complex macromolecular compounds containing not only phosphorus, but also carbon, boron, and nitrogen, for use as a material which will stand high temperatures of about 500°.

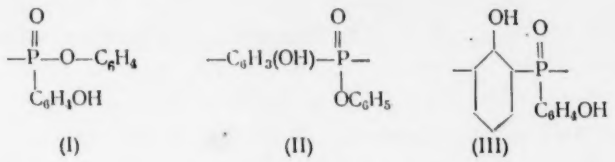
In the present work an attempt was made to synthesize macromolecular compounds of phosphorus from phosphoric anhydride and aluminum phenoxides. Three types of reaction between phosphoric anhydride and organic compounds have been described. The first of these, the reaction of phosphoric anhydride with alcohols or phenols, is the oldest method of preparing phosphoric esters; esters of polyphosphoric acids are obtained as impurity [1, 4]. When alcohols are heated with phosphoric anhydride, a reaction of a different type occurs: dehydration with formation of olefins [5]; it is possible that the reaction proceeds through the intermediate stage of the formation of phosphoric esters. Lecher, Chao, Whitehouse, and Greenwood [6] found yet another type of reaction: at a high temperature (about 270°) phosphoric anhydride reacts with aromatic hydrocarbons or phenol ethers with formation of alkylphosphonic acids, i.e., true organophosphorus compounds. Because of the low yield, the comparatively complicated apparatus, and the occurrence of corrosion, this method was found to be inconvenient from the preparative point of view. Later, the same authors reported that the analogous reaction leading to the formation of arylphosphonothioic acids from phosphorus pentasulfide [7] goes more smoothly. Phenol ethers (anisole and phenetole) react in this way more readily than other compounds.

Aluminum phenoxides should be essentially similar to esters of inorganic acids or even to acid anhydrides. In fact, both aluminum hydroxide and phenols form saltlike compounds with alkalis. Aluminum alkoxides do not decompose on fusion, and many can even be vacuum-distilled without decomposition. Hence, they do not possess the character of ionic compounds, but, on the contrary, are more nearly covalent in nature. It might therefore be supposed that in the reaction of aluminum phenoxides with phosphoric anhydride or phosphorus pentasulfide organophosphorus compounds of the type of hydroxyphenylphosphonic acids would be formed. It was found that, when a mixture of approximately equimolecular amounts of phosphoric anhydride and aluminum phenoxide was heated in presence of a catalytic amount of sodium hydroxide, there was a vigorous exothermic reaction and the mass sintered together. As a result we obtained an organic substance as a white powder, which was noncrystalline, contained phosphorus, and was insoluble in water and organic solvents. The substance dissolved in 5% aqueous sodium hydroxide, and on acidification with sulfuric, hydrochloric, or acetic acid it was again precipitated. By this method the product was readily purified from aluminum phosphate and a small

amount of resinous impurity and other substances. When the alkaline solution was cooled to -2° there was a precipitate of the sodium salt of the substance in the form of long uncolored prisms. Aluminum cresoxides underwent a similar condensation with P_2O_5 with still greater ease. In this case a catalyst (alkali) was unnecessary.

The products of the condensation of aluminum phenoxide and m-cresoxide were investigated; they were insoluble in anything other than aqueous alkalis and pyridine, and when their alkaline solutions were cooled crystalline sodium salts were precipitated. The substances were insoluble in aqueous solution of weak alkalis (sodium carbonate, sodium acetate). All this indicates the probable presence of a phenolic hydroxyl in the substance. Elementary analyses showed that the products obtained in absence of catalyst contained about 14.7% of phosphorus, and those obtained in presence of alkali contained about 12%, i.e., one atom of phosphorus to 1.9-2.2 molecules of phenol. The analyses of the sodium salts of the products were analogous. The product of the condensation of aluminum phenoxide was readily acetylated. According to the hydroxyl value the molecular weight was 254-258. Nitration with a strong nitration mixture gave picric acid, from the phenoxide product, and trinitro-m-cresol from the m-cresoxide products; the final solutions contained phosphoric acid. Strong sulfuric acid split the substance up with formation of a mixture of sulfonic acids and resinous substances. Bromination with excess of bromine in alkaline solution led to the formation of a bromo compound containing about 47% of bromine, similar in properties and appearance to the starting substance. The product of the condensation of P_2O_5 with aluminum phenoxide melted with decomposition above 350°; at 360-400° (1 mm) distillation occurred with decomposition, and a mixture of phosphorus-containing substances with a phosphine odor came over; the product was partly solid.

From a comparison of the analytical data it must be supposed that the product was a polycondensation product; the acetyl value gave the molecular weight of the structural unit of the substance, which, in view of its stability to hydrolysis, was an organophosphorus compound. For the structural unit we may suggest one of the following three isomeric structures of formula $C_{12}H_9O_3P$, mol. wt. 232:



(I) (II) (III)

The product from m-cresol, and also the sodium salts and bromo compounds, will have analogous structures. A comparison of the analytical data with those calculated for the proposed structures is given in the table. The C-P bond may be in the o- or p-position, but not in the m-position. If the bond were in the m-position, destructive nitration could not give picric acid (a product with unsubstituted m-positions). Also, if the bond were in the m-position, the product of condensation with aluminum m-cresoxide would not have been obtained.

The structures (I) and (II) interpret the product as a polyester. The esters of polyphosphoric acids of high molecular weight which have been described in the literature are readily hydrolyzed with water [1], as also are polyalkyl metaphosphates [2]. Tetraethyl pyrophosphate and hexaethyl metaphosphate are hydrolyzed slowly with water, but are readily hydrolyzed with alkalies [8]. No polyphosphoric esters that are stable to the action of alkali are met in the literature. All the substances that we obtained were only slightly resinified even after long (80 hours) boiling with 5-10% sodium hydroxide solution.

However, it cannot be considered that the polyester formulas (I) and (II) are excluded entirely. Some of the inorganic salts of polyphosphoric acids, e.g., Currol's salt [9], which are considered to have three-dimensional structures, are stable to the action of alkalis. Judging from the insolubility which it possessed in spite of its ability to form saltlike compounds, the compound which we obtained was of three-dimensional structure. The possibility cannot be excluded that three-dimensional polyphosphoric esters exist which, like Currol's salt, are stable to the action of alkalis. The poor solubility compels us to suppose that our compounds are indeed of three-dimensional structure. Formula (III) readily explains the stability of the substance to alkalis. It must be supposed that, of the two hydroxyls of the structural unit of (III), only one is reactive. The other is screened by two ortho-substituents and is unreactive, as is usually the case, e.g., in o-di-t-butylphenol [10]. The somewhat

Characteristics of Products of the Condensation of Aluminum Phenoxides with Phosphoric Anhydride

Condensation product	Structural unit	Calculated		Found		
	formula	mol. wt.	P (%)	mol. wt.	P (%)	Br (%)
P_2O_5 and phenoxide	$C_{12}H_9O_3P$	232	12.93 —	254; 258	11.61;11.62 to 14.7	–
Same, as sodium salt	$C_{12}H_8O_3PNa$	254	12.20 —	254; 252.3	12.22	–
Same, brominated	$C_{12}H_5O_3PBr_4$	548	5.49 58.4	—	5.4-5.23	55.8
P_2O_5 and m-cresoxide	$C_{14}H_{13}O_3P$	260	11.92 —	268; 272	12.5; 11.86	–
P_2O_5 and mixture of cresols (tricresol)	$C_{14}H_{13}O_3P$	260	11.92 —		11.9; 11.87	–

high acetyl value is to be explained by the partial acetylation of the second hydroxyl. This formula is more probable than the others.

It is possible that the polycondensation product consists of a mixture of structures. However, the fact that the sodium salt of the substance is crystalline gives us reason to suppose that the structure is comparatively regular and the molecular weight is not very great. The insolubility of the substance made it impossible to carry out many physical determinations, as in the case of other three-dimensional molecules derived from phenols (phenoplasts).

The structure (III) is somewhat similar in configuration to phenol-formaldehyde condensation products. It was found that the copolycondensation of phenol, formaldehyde (in practice paraform was used), aluminum phenoxide, and phosphoric anhydride occurred readily. With equimolecular amounts a homogeneous resin was obtained; this was soluble in alkalis and was reprecipitated with acids, and it corresponds to the compositions of the original reactants in analysis for phosphorus (the phosphorus content was one-half of that of the product of the reaction of P_2O_5 with aluminum phenoxide.

An attempt was made to obtain a cross-linked product of the copolycondensation of aluminum phenoxide, phosphoric anhydride, and Novolak resin. On heating, a very vigorous reaction occurred with the evolution of heat. However, from the resulting solid resin it was possible to extract a phosphorus-containing product with 5% sodium hydroxide. The residue, which did not contain phosphorus, was evidently phenol-aldehyde resin. Hence, in the first attempts we did not succeed in obtaining a cross-linked product.

EXPERIMENTAL

Aluminum phenoxides were prepared by heating the phenol with aluminum turnings in stoichiometric amounts [11], and they were used without further purification.

Condensation of Phosphoric Anhydride with Aluminum Phenoxide. The reaction was carried out in a 100-ml round-bottomed flask fitted with thermometer and reflux air condenser protected by a calcium chloride tube. Phosphoric anhydride (7.1 g, 0.05 mole), aluminum phenoxide (18.3 g, 0.06 mole), and sodium hydroxide powder (1 g) were carefully mixed by shaking in the reaction flask and then cautiously heated on a sand bath. At about 50° an exothermic reaction set in. In ten minutes the temperature of the mixture rose to 255°, and after a further 15 minutes the evolution of heat ceased. The mass was cooled and was extracted with five 50-ml portions of 5% sodium hydroxide solution; after the addition of each portion the flask was shaken mechanically for 30 minutes, the solution was decanted, and the process was repeated. After five extractions almost the whole had gone into solution. The alkaline solutions were combined and filtered from a small amount of precipitate; the filtrate was acidified with 2 N HCl. The white precipitate that formed was filtered off, washed with hydrochloric acid and with water, and dried, at first in air and then at 105°. We obtained 8.1 g of white powder. The substance was insoluble in alcohol, acetone, ether, dioxane, and chloroform; it was soluble in aqueous caustic alkalis, 2-aminoethanol, and pyridine after long heating. It was only slightly soluble in sodium carbonate solution. Found: P 11.62; 11.61%. Hydroxyl value: 157.5; 158.2; 160.8; 161.4; Mol. wt. per 1 OH group: 254; 252.3; 248.8; 247.8.

With increase in the amount of phosphoric anhydride by 20-30%, the yield of product was reduced to 4 g, i.e., it was halved. When the same reaction was carried out without the addition of alkali, from the same amount of reactants we obtained 8 g of a substance with similar properties, but with a higher phosphorus content. Found: P 14.7; 14.7%. However, sometimes the experiments led to the formation of only water-soluble products, i.e., the results were not consistent.

Preparation of sodium salt. A solution of 3 g of the substance in 15 ml of 5% sodium hydroxide was cooled to -3° and kept at this temperature for three hours. The precipitated crystals were filtered off and washed with small amounts of water. We obtained long prisms, m.p. >400° (decomp.). Found: P11.09; 11.61%. A weighed sample of the product was acidified, and the substance obtained was washed and analyzed for hydroxyl value: 154.4; 158.2.

Bromination. A solution of 3 g of the substance in 35 ml of 5% sodium hydroxide solution was cooled to 0° with ice, and 32 g (0.2 mole) of bromine was added dropwise. A precipitate gradually formed. After two hours it was filtered off, washed with water, with 3% sodium carbonate solution, and again with water, and dried: yield 5.4 g. The product was purified by dissolving it in 5% sodium hydroxide solution, filtering the solution, and reprecipitation with 2 N HCl. We obtained a white powder, m.p. >400° (decomp.); it dissolved in pyridine, but was insoluble in benzene, alcohol, and acetone. Found: P5.4; 5.23; Br 47.58; 47.36%.

Nitration. A mixture of 5 g of the substance and 50 ml of 92% sulfuric acid was heated in a water bath until a solution was formed. The solution was cooled to 0°, and at this temperature over a period of 90 minutes 50 ml of nitric acid (sp. gr. 1.4) was added dropwise. The precipitate formed was filtered off, washed with cold water, crystallized from alcohol, and dried. We obtained 4.8 g of picric acid, m.p. 121.5°. The literature [12] gives m.p. 121.8°. Naphthalene picrate, m.p. 150-151°, was prepared. The literature [12] gives m.p. 150.5°.

Apart from nitric and sulfuric acids the mother liquor contained phosphoric acid, which was determined by precipitation with ammonium molybdate after the separation of sulfuric acid as calcium sulfate.

Condensation of Phosphoric Anhydride with Aluminum m-Cresoxide. The reaction was carried out similarly to that with aluminum phenoxide. Phosphoric anhydride (7.2 g, 0.05 mole) and aluminum m-cresoxide (20.5 g, 0.06 mole) were mixed and heated. At 30-40° an exothermic reaction set in, and the temperature of the mixture rose to 260°. The mixture was then cooled and treated as in the case of the condensation of aluminum phenoxide; yield 10.5 g. Found: P 12.5; 12.55%. Hydroxyl value: 145.3; 147.1.

On nitration of 5 g of the substance with the same amounts of reagents and under the same conditions as for the condensation product of aluminum phenoxide, we obtained 4 g of trinitro-m-cresol, m.p. 108.5°. The literature [12] gives m.p. 109.5°.

Condensation of Phosphoric Anhydride with a Mixture of Isomeric Aluminum Cresoxides (from Technical Tricresol). The reaction was carried out in the same way as in the case of aluminum m-cresoxide. The final temperature in the exothermic reaction was 240°. Yield 9.2 g. Found: P 11.9; 11.87%.

Copolycondensation of Aluminum Phenoxide, Phosphoric Anydride, Phenol, and Paraform. A mixture was prepared from 15.5 g (0.05 mole) of aluminum phenoxide, 15.5 g (0.165 mole) of phenol, 4.8 g (0.16 mole) of paraform, and 7.1 g (0.05 mole) of phosphoric anhydride. This was heated in a sand bath until the exothermic reaction began. The temperature rose rapidly to 150°. The mixture was then heated to 200°, cooled, and purified by dissolving it in 5% sodium hydroxide, filtering, and acidifying, as in the experiment with aluminum phenoxide; drying was at 100°. We obtained 12.5 g of reddish-brown powder, m.p. >400°. Found: P 3.97; 3.83%. The product did not burn readily, was insoluble in organic solvents, and was homogeneous: we did not succeed in effecting any separation by extraction with solvents or alkali.

Attempts to Prepare a Cross-Linked Polycondensation Product with Novolak Resin. Novolak resin was prepared by Andrianov and Karandashov's method [13]. Phosphoric anhydride (13.4 g, 0.094 mole), aluminum phenoxide (14.4 g, 0.047 mole), and Novolak resin (5 g) were mixed and heated. There was a vigorous reaction, and the temperature rose to 260°. The substance was purified by dissolving it in 5% sodium hydroxide in the usual way, but only a part of the product dissolved. Acidification of the filtrate gave 4.2 g of product, which scarcely differed in properties and analysis from the product of the condensation of aluminum phenoxide with phosphoric anhydride. Found: P 10.76; 10.97%. Of the original substance, 4.9 g did not dissolve in 5% sodium hydroxide. This material did not contain phosphorus and was probably formed from the Novolak resin.

SUMMARY

1. The condensation of aluminum phenoxide and cresoxides with phosphoric anhydride gave organic compounds of phosphorus which were insoluble in the usual solvents, but soluble in 5% sodium hydroxide and in pyridine.

2. Nitration of the substances synthesized gave trinitrophenol and trinitro-m-cresol, respectively.

3. The "hydroxyl values" of the products were determined by acetylation.

4. The sodium salt and dibromo derivative of the product of the condensation of aluminum phenoxide with phosphoric anhydride were prepared.

5. On the basis of the investigations it is suggested that macromolecular compounds of phosphorus are obtained that contain phenolic hydroxyls; formulas are suggested for these.

6. The copolycondensation of aluminum phenoxide, phosphoric anhydride, phenol, and paraform was carried out.

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CHEMICAL REACTIONS OF DIALKOXYTITANIUM OXIDES

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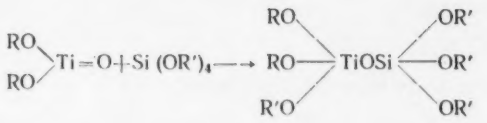
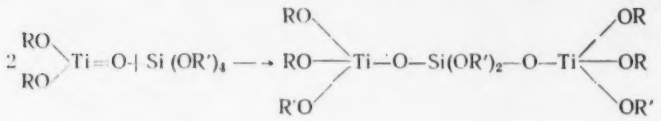
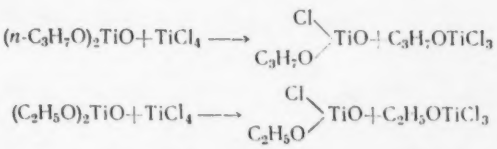
Dialkoxytitanium oxides $(RO)_2TiO$, which we were the first to prepare, have received very little study. We recently succeeded in showing [1] that these compounds are monomeric, at least in dilute solutions. In the same paper we described the reactions of dipropoxy- and diisobutoxy-titanium oxides with tetraalkoxysilanes, which proceed as follows:

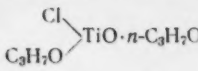




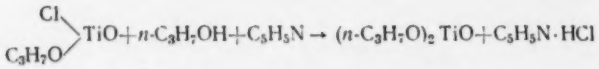
Apart from this, there is no information in the literature about the reactions of this class of substance. In the present paper we report some information on the chemical properties of dialkoxytitanium oxides. We have continued our study of additions at the $>Ti=O$ bond, investigated transesterification and replacement of alkoxyls by halogen, and also discovered the reaction in which oxygen attached to titanium is replaced by two atoms of chlorine.

Alkoxychlorotitanium oxides were prepared from dialkoxytitanium oxides by the action of titanium tetrachloride or acetyl chloride. Two cases of the first reaction were carried out:

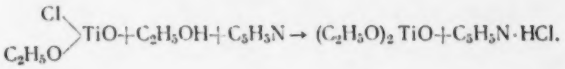


Chloropropoxy- and chloroethoxy-titanium oxides, which are formal analogs of alkyl chloroformates, are solids, very stable to the action of atmospheric moisture, and soluble in alcohols, tetrahydrofuran, and benzene. They form stable compounds with alcohols. Thus, treatment of chloropropoxytitanium oxide with an equimolecular amount of propyl alcohol gave a substance of composition  , a low-melting substance that could be readily crystallized from hexane.

With the object of proving the structure of chloropropoxytitanium oxide, we carried out its alkoxylation with propyl alcohol:

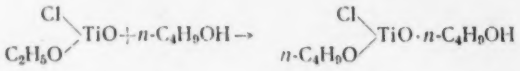


The dipropoxytitanium oxide so obtained was analyzed: its molecular weight was close to the calculated value. With the aid of infrared spectra, it was shown to be identical with the dipropoxytitanium oxide previously obtained by us. Alkoxylation was carried out also in the case of chloroethoxytitanium oxide:



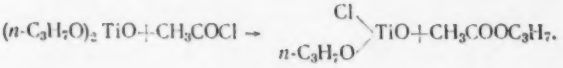
Here we obtained diethoxytitanium oxide.

On the transesterification of chloroethoxytitanium oxide with butyl alcohol

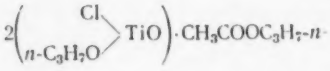


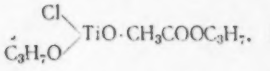
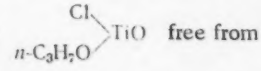
we obtained a crystalline compound of butoxychlorotitanium oxide and butyl alcohol.

The second method of preparing alkoxychlorotitanium oxides, the action of acetyl chloride on dialkoxytitanium oxides, corresponds to the scheme:



The reaction went immeasurably rapidly at about -10°. A compound of composition



was obtained; it was a low-melting substance, readily soluble in the usual organic solvents. The molecular weight of this product, which was determined cryoscopically in benzene, was close to that calculated for the formula 2  . It must be pointed out that the amount of propyl acetate combined with a molecule of chloropropoxytitanium oxide varied somewhat from experiment to experiment. We succeeded in obtaining  free from propyl acetate by this method only after heating the product at a residual pressure of 10^{-5} mm for five hours at a bath temperature of 150-155°.

Quite recently, Razuvaev, Bobinova, and Étlis [2] reported that alkoxytitanium trichlorides containing secondary or tertiary groups are decomposed according to the scheme:

$$C_nH_{2n+1}OTiCl_3 \rightarrow TiOCl_2 + C_nH_{2n} + HCl$$

$$C_nH_{2n} + HCl \rightarrow C_nH_{2n+1}Cl$$

$$mC_nH_{2n} \rightarrow (C_nH_{2n})_m$$

The titanium oxychloride obtained in this way was an infusible, insoluble compound, which we did not succeed in obtaining in a pure state because olefin polymer was firmly adsorbed on its surface. We obtained titanium oxychloride in the form of its double compounds with alcohols $Cl_2TiO \cdot 2n\text{-}C_3H_7OH$ and $Cl_2TiO \cdot 2i\text{-}C_4H_9OH$ by the action of chlorine on dipropoxy- and diisobutoxy-titanium oxides. The reaction products were colorless, readily fusible, crystalline substances, which could be recrystallized from carbon tetrachloride.

The reaction of dialkoxytitanium oxides with chlorine probably goes by the same mechanism as that of the action of halogens on tetraalkoxytitaniums. The proposed mechanism of this reaction (for the case of tetraalkoxytitaniums) has been described previously [3]. It should be noted that both in the action of halogens on titanium ortho esters and also in the action of chlorine on dialkoxytitanium oxides substances are formed in which the titanium must be assumed to have a coordination number of 5 [$(RO)_2TiCl_2 \cdot ROH$ and $Cl_2TiO \cdot 2ROH$].

We studied also the reactions of dipropoxytitanium oxide with dichlorodimethyl- and dichloroethylmethylsilanes. The reactions went as follows:

$$(n\text{-}C_3H_7O)_2TiO + (CH_3)_2SiCl_2 \rightarrow (n\text{-}C_3H_7O)_2TiCl_2 + [(CH_3)_2SiO]_n$$

$$(n\text{-}C_3H_7O)_2TiO + \begin{matrix} CH_3 \\ C_2H_5 \end{matrix}\!\!>\!SiCl_2 \rightarrow (n\text{-}C_3H_7O)_2TiCl_2 + \left[\begin{matrix} CH_3 \\ C_2H_5 \end{matrix}\!\!>\!SiO\right]_n$$

When dichloroethylmethylsilane was taken, the titanium-containing product was isolated as its compound with propyl alcohol. The reaction of tetrapropoxysilane with the compounds of dipropoxytitanium dichloride with propyl alcohol went analogously:

$$Cl_2TiO \cdot 2n\text{-}C_3H_7OH + Si(OC_3H_7)_4 \rightarrow$$

$$\rightarrow Cl_2Ti(OC_3H_7)_2 \cdot n\text{-}C_3H_7OH + n\text{-}C_3H_7OH + [OSi(OC_3H_7)_2]_n.$$

We studied the reaction of dipropoxytitanium oxide with nonyl alcohol:

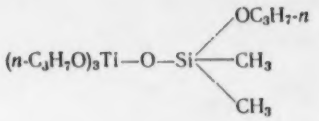
$$(n\text{-}C_3H_7O)_2TiO + 2n\text{-}C_9H_{19}OH \rightarrow (n\text{-}C_9H_{19}O)_2TiO + 2n\text{-}C_3H_7OH.$$

Here a quantitative yield of bisnonyloxytitanium oxide was obtained.

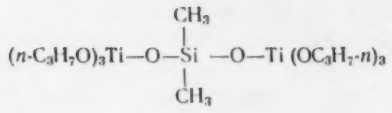
In a futher study of the addition at the Ti = O bond in a dialkoxytitanium oxide molecule, we carried out the reaction of dipropoxytitanium oxide with dimethyldipropoxysilane:

$$(n\text{-}C_3H_7O)_2TiO + (n\text{-}C_3H_7O)_2Si(CH_3)_2 \rightarrow (n\text{-}C_3H_7O)_3Ti\text{-}O\text{-}Si\begin{matrix} \diagup OC_3H_7\text{-}n \\ \text{---} CH_3 \\ \diagdown CH_3 \end{matrix}$$

Here we isolated two substances containing titanium and silicon in the molecule:



and



We carried out also the reaction of diethoxytitanium oxide with tetraethoxytitanium, and it was found that the reaction went in a more complicated fashion: for both 1 : 1 and 2 : 1 reactant ratios we obtained octaeth-oxytrititanoxane (which was shown by the analysis and by the melting point and molecular weight of the reaction product). Here it should be mentioned that in the hydrolysis of tetraethoxytitanium [4, 5] the product was not hexaethoxyditi tanoxane: on treatment of ethyl orthotitanate with water (molar ratio 2 : 1) the product is not hexaethoxyditi tanoxane formed in accordance with the equation

$$2(C_2H_5O)_4Ti + H_2O \longrightarrow (C_2H_5O)_6Ti_2O + 2C_2H_5OH,$$

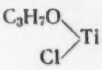
but octaethoxytrititanoxane $(C_2H_5O)_8Ti_3O_2$.

It should be noted that the molecular weights of all the titanium-containing substances described in this paper were determined by the cryoscopic method, and the results are close to the values calculated for the monomeric compounds. The procedure permitting the use of the method of cryoscopy for the determination of molecular weights of titanium-containing organic compounds, which are known to be associated in solutions, was described by two authors of this paper and Dubovitskii [6].

EXPERIMENTAL

All experiments were carried out with completely dry reactants under conditions excluding the access of atmospheric moisture.

Action of Titanium Tetrachloride on Dipropoxytitanium Oxide. A solution of 7.31 g (0.043 mole) of dipropoxytitanium oxide in hexane was introduced into a three-necked flask fitted with stirrer, reflux condenser, and dropping funnel. The reaction flask was cooled with ice and salt and its contents were stirred vigorously while 7.61 g (0.043 mole) of titanium tetrachloride was added slowly dropwise from the dropping funnel. A precipitate formed; stirring was continued in the cold for three hours. The precipitate was filtered off, washed on the filter with five portions of hexane, and dried: first on the filter in a stream of dry air for 90 minutes, and then in a vacuum (1-2 mm, bath temperature 50-60°, one hour). This gave 6.03 g (94%) of a grayish powder, soluble in the cold in ethyl and propyl alcohols, in tetrahydrofuran, and in benzene. In a sealed capillary the substance melted at 92-96°. Found: mol. wt. 153; 157 (cryoscopic method in benzene); calculated 158.5.

Found: C 22.50; 22.55; 21.55; H 4.83; 4.74; 4.53; Ti 30.00; 30.08; 30.40%  Calculated:

C 22.73; H 4.45; Ti 30.22%.

The product of an analogous experiment was purified by precipitating it from tetrahydrofuran solution with hexane. Found: Cl 22.36; 22.17%. C_3H_7OTiO (Cl). Calculated: Cl 22.37%.

From the filtrate and the hexane used for washing the precipitate we distilled off the hexane at a residual pressure of 20-30 mm. A yellow crystalline substance remained in the flask; weight 6.67 g (58%). A part of the substance was sublimed in a vacuum (Found: Ti 22.2; 22.36% $C_3H_7OTiCl_3$. Calculated: Ti 22.45%), and a part was distilled at 12 mm.

The melting point of the distilled sample was 65-68° (in sealed capillary). The literature [7] gives m.p. 65-67°.

Preparation of the Double Compound of Chloropropoxytitanium Oxide and Propyl Alcohol. To a benzene solution of 7.17 g (0.045 mole) of chloropropoxytitanium oxide was added 2.71 g (0.045 mole) of propyl alcohol. On the next morning benzene was distilled off at 25-30 mm. The residue was crystallized twice from hexane. The product was readily soluble in the cold in carbon tetrachloride, alcohols, and benzene, and it dissolved when warmed with hexane; it melted at 99-102° in a sealed capillary. Found: C 33.36; 33.37; H 6.81; 6.88%.

C_3H_7O
Cl$\diagdown$ TiO·C_3H_7OH. . Calculated: C 32.95; H 6.87%. Found: mol. wt. 224; 223 (determined cryoscopically in benzene). Calculated: mol. wt. 218.5.

Alkoxylation of Chloropropoxytitanium Oxide with Propyl Alcohol. A three-necked flask fitted with stirrer, reflux condenser, and dropping funnel was charged with 1 g (0.0126 mole) of pyridine as a solution in 10 ml of benzene and 0.8 g (0.0133 mole) of propyl alcohol. A solution of 2 g (0.0126 mole) of chloropropoxytitanium oxide in 5 ml of benzene and 2.4 g (0.0399 mole) of propyl alcohol was added from the dropping funnel with vigorous stirring and ice-cooling of the flask. Ammonia was passed into the reaction mixture until precipitation was complete (one hour). The precipitated pyridine hydrochloride was filtered off and dried on the filter with a stream of dry air; weight 1 g (69%). Solvent and excess of alcohol were distilled from the filtrate. From the residue we isolated 1.5 g (65.5%) of dipropoxytitanium oxide. Found: C 39.82; 39.62; H 7.75; 7.73; Ti 26.69; 26.84% $(C_3H_7O)_2TiO$. Calculated: C 39.58; H 7.75; Ti 26.30%. Found: mol. wt. 196; 195. Calculated: mol. wt. 182.

Vibration frequencies in the infrared absorption spectra of known diproxytitanium oxide and of the dipropoxytitanium oxide obtained by the alkoxylation of chloropropoxytitanium oxide:

Known sample: 810, 890, 980, 1020, 1050, 1080, 1130, 1250, 1370-1384, 1470

Sample prepared by alkoxylation: 790, 890, 968, 1010, 1053, 1080, 1125, 1250, 1375, 1470

Action of Titanium Tetrachloride on Diethoxytitanium Oxide. The procedure was the same as in the synthesis of chloropropoxytitanium oxide. A solution of 3.70 g (0.0185 mole) of titanium tetrachloride in 5 ml of hexane was added to a solution of 3.0 g (0.0195 mole) of diethoxytitanium oxide in 15 ml of hexane. From the reaction mixture we isolated a substance which was soluble in alcohols and, when warmed, in benzene; m.p. 125-129° (decomp.). The yield was close to the quantitative value. Found: C 16.72; 17.01; H 3.62; 3.58%. C_2H_5OTiO. Calculated: C 16.60; H 3.46%.

|
Cl

Alkoxylation of Chloroethoxytitanium Oxide with Ethanol. A solution of 3.97 g (0.050 mole) of pyridine in 10 ml of benzene and 2.5 g (0.054 mole) of ethanol were introduced into a three-necked flask fitted with stirrer, reflux condenser, and dropping funnel. With vigorous stirring and cooling of the flask with ice, a solution of 6.26 g (0.043 mole) of chloroethoxytitanium oxide in 5.6 g (0.123 mole) of ethanol and 10 ml of benzene was added dropwise from the dropping funnel. Ammonia was passed through the reaction mixture for one hour. The precipitated pyridine hydrochloride was filtered off and dried on the filter with a stream of dry air; weight 3.10 g (53%). Solvent and excess of alcohol were distilled from the filtrate. From the residue we isolated 3.66 g (55%) of diethoxytitanium oxide. Found: C 30.85; 31.15; H 6.03; 6.10; Ti 31.93; 31.55%. $(C_2H_5O)_2TiO$. Calculated: C 31.19; H 6.54; Ti 31.10%.

Transesterification of Chloroethoxytitanium Oxide with Butyl Alcohol. Chloroethoxytitanium oxide (5.4 g) was dissolved in butyl alcohol (56 g). The reaction mixture was heated for one hour at a bath temperature of 70-80°. Ethanol was then gradually distilled off, and the excess of butyl alcohol was driven off at 20-30 mm. The residue, a viscous oil, was heated at 1 mm at a bath temperature of 50-55° for two hours to remove traces

of butyl alcohol. After two days the oil crystallized out. Yield 92%. The product was crystallized three times from hexane; m.p. 73-74°. Found: C 38.99; 38.83; H 7.38; 7.69%. $(C_4H_9O)(Cl)TiO \cdot C_4H_9OH$. Calculated: C 38.94; H 7.70 %. Found: mol. wt. 231; calculated: mol. wt. 246.5.

Action of Acetyl Chloride on Dipropoxytitanium Oxide. A solution of 6.08 g (0.033 mole) of dipropoxytitanium oxide in 20 ml of hexane was introduced into a three-necked flask fitted with stirrer, reflux condenser, and dropping funnel. With stirring and cooling of the flask with ice, a solution of 2.58 g (0.033 mole) of acetyl chloride in 20 ml of hexane was added slowly. The reaction mixture was stirred at room temperature for 30 minutes. After some time a viscous oil was precipitated, and this was separated and heated at a bath temperature of 50-60°, first at 10-15 mm and then at 2 mm, to remove traces of solvent. The residue amounted to 2.52 g. After the removal of hexane we isolated a further 4.24 g of product. The substance was purified by precipitating from its solution in carbon tetrachloride (with an addition of 2.57 g of propyl acetate) by means of hexane; m.p. 78-84°. Found: C 30.66; 30.68; H 5.74; 5.73%. $2[(C_3H_7O)(Cl)TiO] \cdot CH_3COOC_3H_7$. Calculated: C 31.50; H 5.72%. The chlorine content was determined on a separate sample. Found: Cl 16.57; 16.65%. Calculated %: Cl 16.90; Found: mol. wt. 249; 228. Calculated: mol. wt. 209.5.

Action of Chlorine on Dipropoxytitanium Oxide. A solution of 16.24 g (0.0895 mole) of dipropoxytitanium oxide in 60 ml of petroleum ether was introduced into a three-necked flask fitted with stirrer, reflux condenser, and tube for the passage of gas and surrounded with a bath at 0°. Chlorine was passed through the solution until a turbidity appeared (two hours). Addition was then made of 5.35 g (0.0895 mole) of propyl alcohol. There was a colorless crystalline precipitate. When dried with a stream of dry air it weighed 22.5 g (98.5%). The product was crystallized from carbon tetrachloride; m.p. 86-87°. Found: C 27.94; 27.96; H 6.38; 6.48; Ti 19.05; 19.05%. $Cl_2TiO \cdot 2C_3H_7OH$. Calculated: C 28.23; H 6.27; Ti 18.82%. Found: mol. wt. 265; 253. Calculated: mol. wt. 255.

Action of Chlorine on Diisobutoxytitanium Oxide. The procedure was as in the preceding experiment. A stream of chlorine was passed for 2.5 hours through a solution of 22 g of diisobutoxytitanium oxide in 30 ml of petroleum ether. On the next morning the precipitate that had formed was filtered off. It was crystallized from carbon tetrachloride; yield 10 g (34%); m.p. 92-94°. Found: C 33.49; 33.49; H 6.98; 7.28; Cl 25.25; 24.97; Ti 16.67; 16.41%. $Cl_2TiO \cdot 2C_4H_9OH$. Calculated: C 33.94; H 7.12; Cl 25.05; Ti 16.92.

Reaction of Dipropoxytitanium Oxide with Dichlorodimethylsilane. To 15.79 g (0.087 mole) of dipropoxytitanium oxide we added 11.52 g (0.089 mole) of dichlorodimethylsilane; the mixture became warm. The contents of the flask were heated at a bath temperature of 100° for one hour. After some time the liquid separated into layers. The lower layer, which was extremely viscous and immediately began to decompose under the action of atmospheric moisture, was distilled at 121-123° (0.5 mm). Because of the viscosity and instability of the substance we were able to determine the refractive index only tentatively: n_D^{20} 1.575. Found: C 30.05; 29.65; H 5.63; 5.89; Cl 29.94; 30.03%. $(C_3H_7O)_2TiCl_2$. Calculated: C 30.39; H 5.90; Cl 29.90%.

The upper layer was a colorless oil and was washed twice with water to decompose dissolved dichlorodipropoxytitanium. It was distilled at 10^{-5} mm; the product came over slowly over a wide range of temperatures (190-225°), but the refractive index scarcely changed from the first to the last distillate (from n_D^{20} 1.4065 to 1.4070). Found: C 32.61; 32.76; H 8.53; 8.29; Si 38.18; 38.07%. $(CH_3)_2SiO$. Calculated: C 32.38; H 8.15; Si 37.88%. Yield 5.45 g (84%). Found: mol. wt. 1800 (determined ebullioscopically in benzene). Calculated: mol. wt. 74.18 (for monomer).

Reaction of Dipropoxytitanium Oxide with Dichloroethylmethylsilane. To 15.7 g (0.0865 mole) of dipropoxytitanium oxide we added 12.2 g (0.0855 mole) of dichloroethylmethylsilane. The reaction mixture was heated for 90 minutes at a bath temperature of 100°, and then 5.1 g (0.0855 mole) of propyl alcohol was added. After some time the reaction mixture solidified. The product was recrystallized from ethanol. Found: C 36.24; 36.39; H 7.67; 7.72; Ti 16.16; 16.12; Cl 23.59; 22.94%. $(C_3H_7O)_2TiCl_2 \cdot C_3H_7OH$. Calculated: C 36.36; H 7.46; Ti 16.13; Cl 23.90%. Yield of recrystallized product 69%. From the mother liquor, after washing it until reac-

tions for titanium and halogen were negative, we isolated a colorless oil. Two distillations at 10^{-5} mm gave a liquid which slowly distilled over a wide range of temperature (above 200°). Found: C 40.97; 40.97; H 9.07; 9.25; Si 31.71;32.03%. $\begin{matrix} C_2H_5 \\ CH_3 \end{matrix}\!\!>\!\!SiO$. Calculated: C 40.86; H 9.15; Si 31.85%. Found: mol. wt. 830 (determined ebullioscopically in benzene). Calculated: mol. wt. 88 (for monomer).

Reaction of Tetrapropoxysilane with the Double Compound of Dichlorotitanium Oxide with Propyl Alcohol. To 14 g (0.055 mole) of the compound of dichlorotitanium oxide with propyl alcohol we added 17 g (0.064 mole) of tetrapropoxysilane. The mixture was heated for one hour at a bath temperature of 100-105°. On cooling, crystals were precipitated (yield 72%) and were crystallized twice from hexane. Found: C 36.68; 36.34; H 7.87; 7.54%. $(C_3H_7O)_2TiCl_2 \cdot C_3H_7OH$. Calculated: C 36.36; H 7.46%. By a polarographic method the titanium content was determined on a separate sample. Found: Ti 16.00; 16.22%; Calculated: Ti 16.13%.

From the filtrate we isolated 2.08 g of propyl alcohol, which corresponded in all its constants to the alcohol taken for the preparation of dipropoxytitanium oxide.

Preparation of Bisnonyloxytitanium Oxide. A solution of 5.79 g of dipropoxytitanium oxide in 13.77 g of nonyl alcohol was heated for 45 minutes at a bath temperature of 100-110°, and then a mixture of propyl and nonyl alcohols was slowly distilled off at a residual pressure of 20-25 mm. A further 13.77 g of nonyl alcohol was added to the reaction mixture, and a mixture of alcohols was slowly distilled off at 3 mm. The last operation was repeated twice further. The residue remaining in the flask after the removal of the alcohols was heated at a bath temperature of 100°, first at 1-2 mm and then at 10^{-5} mm, to remove traces of nonyl alcohol. Found: C 61.65; 61.11; H 10.97; 10.95; Ti 13.44; 13.63%. $(C_9H_{19}O)_2TiO$. Calculated: C 61.70; H 10.93; Ti 13.70%. Yield quantitative; n_D^{20} 1.5109. Found: mol. wt. 378; 322 (determined cryoscopically in benzene). Calculated: mol. wt. 350.

Reaction of Dipropoxytitanium Oxide with Dimethyldipropoxysilane. A solution of 16.31 g (0.089 mole) of dipropoxytitanium oxide and 15.80 g (0.089 mole) of dimethyldipropoxysilane in hexane was boiled for four hours. After distillation of solvent and unchanged dimethyldipropoxysilane from the reaction mixture, two products were isolated from the reaction mixture by distillation at 10^{-5} mm. The first product was a mobile liquid, n_D^{20} 1.5135. Found: C 47.17; 47.32; H 9.21; 9.44%. $(C_3H_7O)_3Ti{-}O{-}Si(OC_3H_7)(CH_3)(CH_3)$. Calculated: C 46.92; H 9.56%. Found: mol. wt. 341; 360. Calculated: mol. wt. 358.4.

When attempts were made to distill the product at a residual pressure of 1 mm, it decomposed. We then isolated propyl orthotitanate; b.p. 140-141° (1.5-2 mm); n_D^{20} 1.4979. The literature [8] gives: b.p. 135-136° (1 mm); n_D^{20} 1.4979.

The second product was a very viscous liquid; n_D^{20} 1.5310. Found: C 44.34; 44.40; H 8.94; 8.88%. $(C_3H_7O)_3TiOSi(CH_3)_2OTi(OC_3H_7)_3$. Calculated: C 44.44; H 8.59%. Found: mol. wt. 573; calculated: mol. wt. 541.

Reaction of Diethoxytitanium Oxide with Tetraethoxytitanium at a Reactant Ratio of 1 : 1. A solution of 14.8 g (0.064 mole) of tetraethoxytitanium in 20 ml of hexane was added to 10.0 g (0.064 mole) of diethoxytitanium oxide. The reaction mixture was heated for 2.5 hours at a bath temperature of 65-70°; hexane was distilled off, and the residue was crystallized from ethanol; yield 44%. Found: C 36.11; 35.92; H 7.59; 7.63; Ti 26.49; 26.62%; $(C_3H_5O)_8Ti_3O_2$. Calculated: C 35.82; H 7.52; Ti 26.81%. M. p. 93-101°. The literature [4] gives m.p. 90-100°. Found: mol. wt. 556; 526.8. Calculated: mol. wt. 536.

Reaction of Diethoxytitanium Oxide with Tetraethoxytitanium at a Reactant Ratio of 2 : 1. To a solution of 5.84 g (0.0379 mole) of diethoxytitanium oxide in a mixture of benzene and petroleum ether we added 4.32 g (0.0189 mole) of tetraethoxytitanium. The reaction mixture was heated at a bath temperature of 80-90° for 90 minutes; solvent was distilled off, and the residue was crystallized from ethanol. Yield 4.2 g (42%). Found: C 35.78; 35.77; H 7.54; 7.36; Ti 26.65; 26.63%. $(C_2H_5O)_8Ti_3O_2$. Calculated: C 35.82; H 7.52; Ti 26.81%.

M. p. 93-98°. The literature [4] gives m.p. 90-100°. Found: mol. wt. 516; 555 (determined cryoscopically in benzene). Calculated: mol. wt. 536.

SUMMARY

1. The first members of a previously unknown class of titanium-containing organic compounds were prepared: chloroethoxy-, chloropropoxy-, and butoxychloro-titanium oxides.

2. By the action of chlorine on diproproxy- and diisobutoxy-titanium oxides, compounds of the following compositions were obtained: $Cl_2TiO \cdot 2n\text{-}C_3H_7OH$ and $Cl_2TiO \cdot 2i\text{-}C_4H_9OH$.

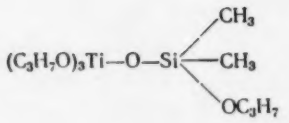
3. By the reaction of dialkyldichlorosilanes with dialkoxytitanium oxides, doubly bound oxygen is replaced by two chlorine atoms:

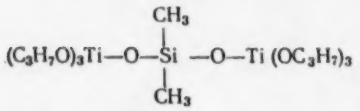
$$(n\text{-}C_3H_7O)_2TiO + Cl_2SiR_2 \rightarrow (n\text{-}C_3H_7O)_2TiCl_2 + [OSiR_2]_x$$

An analogous reaction occurs when tetrapropoxysilane acts on the compound $Cl_2TiO \cdot 2n\text{-}C_3H_7OH$

$$Cl_2TiO \cdot 2n\text{-}C_3H_7OH + (C_3H_7O)_4Si \rightarrow Cl_2Ti(OC_3H_7)_2 \cdot n\text{-}C_3H_7OH + n\text{-}C_3H_7OH + [OSi(OC_3H_7\text{-}n)_2]_x$$

4. The addition of dimethyldipropoxysilane to dipropoxytitanium oxide gives substances of structure:





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ACTION OF NITRIC ACID ON COMPOUNDS CONTAINING THE $CCl_2 = CCl$ GROUP

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We have previously shown that the reaction of anhydrous nitric acid with compounds containing the trichloromethyl group gives carboxylic acids having the same number of carbon atoms in the molecule as the original trichloromethyl compound [1]. It is known that the action of concentrated sulfuric acid both on compounds containing the CCl_3 group and also on compounds containing the $CCl_2 = CH$ group leads to the formation of the corresponding carboxylic acids. Unlike sulfuric acid, with compounds containing the $CCl_2 = CH$ group nitric acid reacts with the formation mainly of neutral products, but also of α-chloro carboxylic acids in 10-16% yield [2].

The action of nitric acid on compounds containing the $CCl_2 = CCl$ group has been described in the literature for the case of simple haloethylenes, and only tetrachloroethylene and tetrabromoethylene give products of an acidic character [3, 4]. Trichloroethylene, heated with concentrated nitric acid, gives mainly dichlorodinitromethane and a little chloropicrin [5].

We investigated the behaviors of 1, 1, 2, 4-tetrachloro-1-butene, 1, 1, 2, 5-tetrachloro-1-pentene, 1, 1, 2, 6-tetrachloro-1-hexene, 1, 1, 2,7-tetrachloro-1-heptene, and 1,1,2,8-tetrachloro-1-octene toward anhydrous nitric acid. Starting compounds of the even series were prepared by the telomerization of ethylene with tetrachloroethylene under the conditions described by Nesmeyanov, Freidlina, and Belyavskii [6]. 1,1,2,5-Tetrachloro-1-pentene and 1,1,2,7-tetrachloro-1-heptene were prepared from 1,1,1,5- and 1,1,1,7-tetrachloroalkanes by a series of transformations [7] (dehydrochlorination, chlorination, and then dehydrochlorination of the products).

We found that nitric acid of sp. gr. 1.517 reacts with the above-cited unsaturated polychloro hydrocarbons, which contain the trichlorovinyl group, already in the cold; much heat is evolved and oxides of nitrogen are liberated. As a result we obtained satisfactory yields of 2,2,4-trichlorobutyric, 2,2,5-trichlorovaleric, 2,2,6-trichlorohexanoic, 2,2,7-trichloroheptanoic, and 2,2,8-trichlorooctanoic acids. In addition to the acids, we observed the formation of small amounts of neutral substances whose structures we did not establish.

The acids synthesized were characterized by the preparation of their acid chlorides, amides, and – for some of the acids – their anilides and ethyl esters. All the amides obtained were crystalline substances. Of the trichloro carboxylic acids named above, only 2,2,4-trichlorobutyric [8] and 2,2,5-trichlorovaleric [9] acids were described in the literature.

2,2,5-Trichlorovaleric acid was prepared by the conjugated chlorination of 1,1,2,5-tetrachloro-1-pentene in acetic acid in presence of mercuric acetate. In their constants the acids prepared from 1,1,2,5-tetrachloro-1-pentene by conjugated chlorination and by the action of nitric acid were identical. The 2,2,4-trichlorobutyric acid that we obtained was a liquid; the 2,2,4-trichlorobutyric acid described in the literature was a

crystalline substance of m.p. 73-75°. In view of this contradiction we synthesized 2,2,4-trichlorobutyric acid by the oxidation of 1,1,2,4-tetrachloro-1-butene with oxygen at 140-150° under ultraviolet radiation. The acid obtained in this way was found to be identical with that obtained by the action of nitric acid on tetrachlorobutene.

It is known that the oxidation of compounds containing $CCl_2 = CH$ [10] or $CCl_2 = CCl$ [11] groups with oxygen leads to α-chloro or α,α-dichloro carboxylic acids. It is probable that the solid trichlorobutyric acid had a different structure; it was prepared by the addition of hydrogen chloride to 2,4-dichlorocrotonaldehyde with subsequent oxidation of the trichlorobutyraldehyde with nitric acid [8]. In assigning the structure of 2,2,4-trichlorobutyric acid to the product the author assumes that the addition of hydrogen chloride to dichlorocrotonaldehyde went contrary to Markovnikov's rule in its generalized form, which is doubtful.

EXPERIMENTAL

Action of Nitric Acid on 1,1,2,4-Tetrachloro-1-butene. The tetrachlorobutene (50 g) was added with stirring and cooling to 50 ml of nitric acid of sp.gr. 1.517. The reaction mixture was heated for one hour at 45-50°, and was then decomposed with water and extracted with ether. The ether extract was washed with water and with a solution of sodium carbonate to separate acidic products. The acid fraction (30.2 g) was distilled and gave 26.3 g (53%) of 2,2,4-trichlorobutyric acid, b.p. 92-101° (1.5 mm) and n_D^{20} 1.4913. After redistillation it had: b.p. 92° (1 mm); n_D^{20} 1.4922; d_4^{20} 1.5092. Found MR 36.82; calculated MR 36.82. Found: C 24.95; 25.04; H 2.63; 2.55%. $C_4H_5Cl_3O_2$. Calculated: C 25.09; H 2.63%.

2,2,4-Trichlorobutyryl chloride was prepared by the action of PCl_5 on the acid and had: b.p. 83° (20 mm); n_D^{20} 1.4895; d_4^{20} 1.5008. Found MR 40.40; calculated MR 40.52.

The anilide had m.p. 90° (from heptane). Found: C 44.94; 44.93; H 3.64; 3.50; N 5.69; 5.60%. $C_{10}H_{10}Cl_3NO$. Calculated: C 45.05; H 3.79; N 5.25%.

The amide had m.p. 54-55° (from heptane). Found: C 25.18; 25.16; H 3.31; 3.21; N 7.47; 7.65%. $C_4H_6Cl_3NO$. Calculated: C 25.22; H 3.18; N 7.35%.

The ethyl ester had: b.p. 78° (6 mm); n_D^{20} 1.4679; d_4^{20} 1.3312. Found MR 45.83; calculated MR 46.04. Found: C 32.22; 32.09; H 3.85; 3.88%. $C_6H_9Cl_3O_2$. Calculated: C 32.83; H 4.13%.

For ethyl 2,2,4-trichlorobutyrate the literature [12] gives: b.p. 62-64° (2 mm); n_D^{20} 1.4680; d_4^{20} 1.3080.

Action of Nitric Acid on 1,1,2,5-Tetrachloro-1-pentene. The procedure was as in the preceding experiment. For reaction we took 47.7 g of the tetrachloropentene and 47 ml of nitric acid. Distillation of the acid fraction (17 g) gave 13.2 g (30%) of 2,2,5-trichlorovaleric acid; b.p. 131-133° (4 mm); n_D^{20} 1.4948; d_4^{20} 1.4519. After redistillation the acid had: b.p. 113-118° (2 mm); n_D^{20} 1.4945; d_4^{20} 1.4480. Found MR 41.34; calculated MR 41.43. Found: C 29.19; 29.31; H 3.72; 3.71%. $C_5H_7Cl_3O_2$. Calculated: C 29.22; H 3.43%. For 2,2,5-trichlorovaleric acid the literature [8] gives: b.p. 117° (2mm); n_D^{20} 1.4950; d_4^{20} 1.4475.

Its acid chloride had: b.p. 117-119° (21 mm); n_D^{20} 1.4920; d_4^{20} 1.4422. Found MR 45.05; calculated MR 45.14.

Its amide had m.p. 46° (from heptane + benzene). Found: C 29.36; 29.36, H 3.64; 3.91; N 6.86; 6.70%. $C_5H_8Cl_3NO$. Calculated: C 29.36; H 3.94; N 6.85%. We obtained also 13.2 g of a neutral fraction.

Action of Nitric Acid on 1,1,2,6-Tetrachloro-1-hexene. For reaction we took 41 g of the tetrachlorohexene and 40 ml of nitric acid. The experimental conditions were as described for the first experiment. Distillation of the acid fraction (27.5 g) gave 24.9 g of 2,2,6-trichlorohexanoic acid; b.p. 123-132° (1.5 mm); n_D^{20} 1.4929. On standing the acid crystallized out. Yield 61%. After recrystallization from heptane, m.p. 46°. Found: C 32.54; 32.50; H 4.12; 4.12%. $C_6H_9Cl_3O_2$. Calculated: C 32.83; H 4.13%.

Its acid chloride had: b.p.94° (3 mm); n_D^{20} 1.4906; d_4^{20} 1.3849. Found MR 49.72; calculated MR 49.75.

Its amide had m.p. 64-65° (from heptane). Found: C 32.85; 32.85; H 4.53; 4.46; N 6.34; 6.52%. $C_6H_{10}Cl_3NO$. Calculated: C 32.98; H 4.61; N 6.41%.

Its anilide had m.p. 69° (from heptane). Found: C 49.11; 49.09; H 4.77; 4.81; N 4.90; 4.89%. $C_{12}H_{14}Cl_3NO$. Calculated: C 48.92; H 4.79; N 4.75%.

Its ethyl ester had: b.p. 112° (3 mm); n_D^{20} 1.4710; d_4^{20} 1.2518. Found MR 55.28; calculated MR 55.40. Found: C 38.53; 38.57; H 5.15; 5.15%. $C_8H_{13}Cl_3O_2$. Calculated: C 38.81; H 5.29%. For ethyl 2,2,6-trichlorohexanoate the literature [12] gives: b.p. 104-108° (3 mm); n_D^{20} 1.4748; d_4^{20} 1.272.

We isolated also 8.3 g of a neutral fraction, which was not investigated.

Action of Nitric Acid on 1,1,2,7-Tetrachloro-1-heptene. Under the conditions described above, from 49.2 g of the tetrachloroheptene we obtained 35 g (72%) of 2,2,7-trichloroheptanoic acid. After redistillation: b.p. 140-142° (1 mm); n_D^{20} 1.4905; d_4^{20} 1.3335. Found MR 50.63; calculated MR 50.66. Found: C 35.98; 35.97; H 5.05; 5.06%. $C_7H_{11}Cl_3O_2$. Calculated: C 36.00; H 4.75%.

2,2,7-Trichloroheptanoyl chloride had: b.p. 83-84° (1 mm); n_D^{20} 1.4880; d_4^{20} 1.3383. Found MR 54.24; calculated MR 54.01.

Its amide had m.p. 61° (from heptane). Found: C 35.91; 36.03; H 5.09; 5.16; N 6.02; 6.01%. $C_7H_{12}Cl_3ON$. Calculated: C 36.15; H 5.20; N 6.02%. From the reaction mixture we obtained 3.2 g of a neutral fraction.

Action of Nitric Acid on 1,1,2,8-Tetrachloro-1-octene. Under the conditions described for the first experiment, from 49.6 g of the tetrachloro-1-octene* we obtained 32.1 g of acid products, from which we isolated 14.1 g (28%) of 2,2,8-trichlorooctanoic acid; b.p. 136-139° (1 mm); n_D^{20} 1.4898; d_4^{20} 1.2940. Found MR 55.29; calculated MR 55.38. Found: C 38.42; 38.28; H 5.43; 5.36%. $C_8H_{13}Cl_3O_2$. Calculated: C 38.81; H 5.29%. We obtained 11.0 g of residue, and esterification of this residue with ethanol gave 4.8 g of ethyl 2,2,8-trichlorooctanoate; b.p. 112° (0.5 mm); n_D^{20} 1.4700; d_4^{20} 1.1898. Found MR 64.63; calculated MR 64.63. Found: C 43.73; 43.81; H 6.12; 6.06%. $C_{10}H_{17}Cl_3O_2$. Calculated: C 43.58; H 6.21%. The total yield of the trichlorooctanoic acid was 37%.

2,2,8-Trichlorooctanoyl chloride had: b.p. 171-173° (3 mm); n_D^{20} 1.4870; d_4^{20} 1.3004. Found MR 58.83; calculated MR 58.99.

Its amide had m.p. 38-39° (from heptane). Found: C 38.69; 38.77; H 5.74; 5.64; N 5.69; 5.70%. $C_8H_{14}Cl_3NO$. Calculated: C 38.97; H 5.72; N 5.68%.

Its anilide had m.p. 53-54° (from heptane). Found: C 51.87; 52.05; H 5.59; 5.64; N 4.30; 4.40%. $C_{14}H_{18}Cl_3NO$. Calculated: C 52.11; H 5.62; N 4.34%.

Oxidation of 1,1,2,4-Tetrachloro-1-butene with Oxygen. On oxidation of 62.2 g of the tetrachlorobutene with oxygen at 140-150° under ultraviolet radiation we obtained 17 g of 2,2,4-trichlorobutyric acid, b.p. 100-110° (2 mm), which after redistillation (15.5 g, 25% yield) had: b.p. 91-94° (1 mm); n_D^{20} 1.4938; d_4^{20} 1.5147. The amide had m.p. 54-55°, undepressed by admixture of 2,2,4-trichlorobutyramide prepared by the action of nitric acid on 1,1,2,4-tetrachloro-1-butene.

SUMMARY

1. Under the action of concentrated nitric acid, compounds containing the $CCl_2 = CCl$ group are smoothly converted into α,α,ω-trichloro carboxylic acids. In this way we prepared 2,2,4-trichlorobutyric, 2,2,5-trichlorovaleric, 2,2,6-trichlorohexanoic, 2,2,7-trichloroheptanoic, and 2,2,8-trichlorooctanoic acids.

2. 1,1,2,4-Tetrachloro-1-butene was oxidized with oxygen under ultraviolet radiation with formation of 2,2,4-trichlorobutyric acid.

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*In this case we took for investigation the wide tetrachlorooctene fraction obtained by the telomerization of ethylene with tetrachloroethylene [6].

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*Original Russian pagination. See C. B. translation.

ACTION OF DIETHYL PHOSPHITE ON p-BENZOQUINONE AND 1,4-NAPHTHOQUINONE

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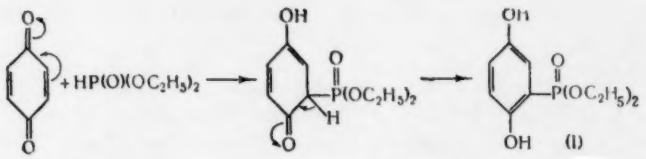
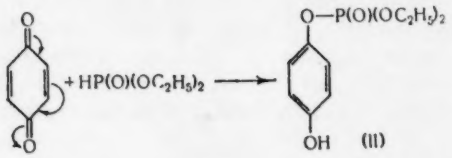
Under the action of basic catalysts, dialkyl phosphites add to α,β-unsaturated ketones [1]. It would be expected that similar addition would occur to p-quinones. It is stated in the patent of Ladd and Harvey [2] that heating of p-quinones with dialkyl phosphites in presence of basic catalysts leads to addition products which probably have the structure of dihydroxyphenylphosphonic esters. For p-benzoquinone the product of equimolecular addition to diethyl phosphite is described as a yellow liquid of n_D^{20} 1.4492. The product of the addition of diethyl phosphite to 1,4-naphthoquinone has m.p. 97-99°.

The addition of dialkyl phosphites to p-quinones may be represented by the scheme:



There is, however, another possible way for dialkyl phosphites to react with quinones:



The possibility of this type reaction is indicated by the reactions of triphenylphosphine [3] and trialkyl phosphites [4] with quinones. Diefenbach [5] states that dialkyl hydroxyaryl phosphates are obtained by the action of dialkyl phosphites on quinones in presence of alkali-metal alkoxides and triethylamine.

In the present paper we report some results obtained on the reactions of p-benzoquinones and of 1,4-naphthoquinone with diethyl phosphite in presence of a sodium alkoxide. In the case of p-benzoquinone we obtained a product which could be distilled in a high vacuum. The compound isolated was an almost colorless viscous

liquid having the following constants: I) b.p. 172.5-173° (0.01 mm); n_D^{20} 1.5025; d_0^{20} 1.2273; II) b.p. 171-174° (0.01 mm); n_D^{20} 1.5020; d_0^{20} 1.2313. Found: MR 59.26; 59.02. $C_{10}H_{15}O_5P$. Calculated: MR 58.81.

Acetylation of the product with acetyl chloride and molecular distillation of the product, followed by distillation in high vacuum, gave a compound with the following constants: b.p. 113-115° (0.035 mm); n_D^{20} 1.4841; d_{20}^{20} 1.2049; Found MR 68.67. $C_{12}H_{17}O_6P$. Calculated MR 68.17.

In analysis the product corresponded to p-acetoxyphenyl diethyl phosphate.* Its hydrolysis with hydrochloric acid gave hydroquinone and phosphoric acid. The ready hydrolysis of the product of the addition of diethyl phosphite to p-benzoquinone into hydroquinone and phosphoric acid and its conversion into a monoacetic ester, and not a diacetic ester as would be expected if it had the structure (I), indicates that it is a phosphoric ester (II).

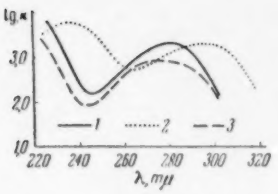


Fig. 1. Ultraviolet spectra of solutions in methanol: 1) product of the addition of diethyl phosphite to p-benzoquinone; 2) ditto, with the addition of CH_3ONa; 3) product of the addition of diethyl phosphorochloridate to hydroquinone.

We made an attempt to synthesize the ester (II) by the action of diethyl phosphorochloridate on hydroquinone in presence of triethylamine. Distillation in high vacuum gave fractions close in analysis to the expected monoester (II). Fraction I had b.p. 148-157° (0.01 mm); n_D^{20} 1.4981; d_0^{20} 1.2176; Found MR 59.29. $C_{10}H_{15}O_5P$. Calculated MR 58.81. Fraction II had b.p. 156-159° (0.01 mm); n_D^{20} 1.4857; d_0^{20} 1.2180; Found MR 58.01. $C_{10}H_{15}O_5P$. Calculated MR 58.81.

However, the higher-boiling fraction, which was close in boiling point, contained considerably more phosphorus. It clearly contained the hydroquinone diester and diethyl phosphate. The monoester formed was readily hydrolyzed to hydroquinone and phosphoric acid. The ultraviolet absorption spectra of methanolic solutions of the product of the addition of diethyl phosphite to p-benzoquinone and of the fraction corresponding to the monoester (II) obtained by the action of diethyl phosphorochloridate on hydroquinone** are shown in Fig. 1 and are similar in character (Curves 1 and 3 respectively). In presence of sodium alkoxide there is a displacement of the absorption toward the longer waves with preservation of the similarity in the character of the spectra (Curve 2), and an absorption maximum appears in the region of 240 mμ. The similarity of the absorption spectrum in presence of alkoxide to the spectrum of hydroquinone [6] points to the possibility that the product is hydrolyzed in an alkaline medium.

Hence, the results show that the product of the addition of diethyl phosphite to p-benzoquinone is diethyl p-hydroxyphenyl phosphate (II).

In the reaction of diethyl phosphite with 1,4-naphthoquinone in dioxane we isolated an addition product in the form of colorless crystals, m.p. 101-102°***. Its ultraviolet absorption spectrum is shown in Fig. 2. Comparison of the ultraviolet spectra of methanolic solutions of the product (Curve 1) and of 1,4-naphthalenediol (Curve 3) shows that the introduction of the phosphoric ester group, as in the case of the product of the addition of diethyl phosphite to p-benzoquinone (see Fig. 1), displaces absorption in the direction of the shorter wave. In an alkaline medium the spectrum of (III) (Curve 2) is close to that of 1,4-naphthalenediol (Curve 3), which indicates the occurrence of hydrolysis. On its hydrolysis with hydrochloric acid, 1,4-naphthalenediol and phosphoric acid were obtained. Acetylation of the product of m.p. 101-102° with acetyl chloride gave the monoacetic ester: b.p. 199-202° (0.3 mm); n_D^{20} 1.5383; d_0^{20} 1.2277; Found MR 86.24. $C_{16}H_{19}O_6P$. Calculated MR 86.33.**** Its absorption spectrum is shown in Fig. 3, which shows that the spectrum of the monoacetic ester of (III) is similar in character to that of the monoacetic ester of the product (II) of the addition of diethyl phosphite to p-benzoquinone (Curve 2) and also to that of the diacetic ester of hydroquinone [6].

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*It must be pointed out that the acetylation does not go smoothly, and on distillation of the reaction products, particularly without preliminary molecular distillation, crystals of hydroquinone diacetic ester, m.p. 121°, are formed.

**The preparation was not analytically pure.

***With ferric chloride in alcoholic solution it gives a cherry-red color, which passes into lilac.

****Exaltation due to the naphthalene ring: 2.82.

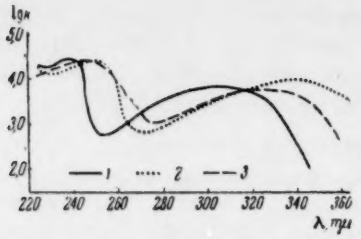


Fig. 2. Ultraviolet absorption spectra of methanolic solutions: 1) product of the reaction of diethyl phosphite with 1,4-naphthoquinone; 2) the same, with the addition of CH_3ONa; 3) 1,4-naphthalenediol.

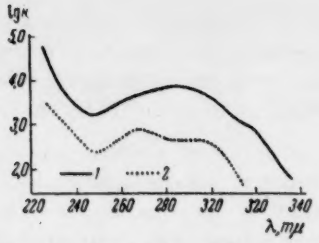
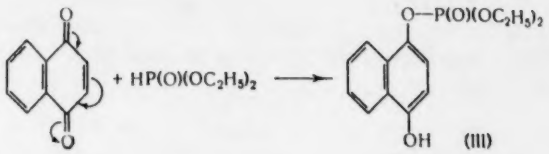


Fig. 3. Ultraviolet absorption spectra of methanolic solutions of monoacetic esters of products of the addition of diethyl phosphite to 1) 1,4-naphthoquinone; 2) p-benzoquinone.

On hydrolysis of the acetic ester we obtained 1,4-naphthalenediol and phosphoric acid. The formation of a monoacetic ester and the readiness of hydrolysis to 1,4-naphthalenediol indicate the structure of the product of mp. 101-102° to be diethyl 4-hydroxy-1-naphthyl phosphate.



(III)

Attempts to synthesize the ester by the action of diethyl phosphorochloridate on 1,4-naphthalenediol were not successful. We obtained a resinous mass which we could not distill in a high vacuum. Hence, our experimental results indicate that the addition of diethyl phosphite, both in the case of p-benzoquinone and in the case of 1,4-naphthoquinone leads to the formation of a mixed ester of ethyl alcohol and the diol with phosphoric acid.

EXPERIMENTAL

Action of Diethyl Phosphite on p-Benzoquinone. Fifteen drops of a saturated solution of sodium methoxide in alcohol were added one at a time to a mixture of 7 g of p-benzoquinone and 9 g of diethyl phosphite. On the addition of each drop there was a rise of temperature. The mixture was heated in a water bath at about 95° for three hours. The resulting thick dark-colored mass was neutralized with acetic acid and distilled in a high vacuum. Distillation gave an almost colorless viscous liquid (9.3 g); this included 2.5 g of b.p. 172.5-173° (0.01 mm); n_D^{20} 1.5025; d_0^{20} 1.2273. Found MR 59.26. $C_{10}H_{15}O_5P$. Calculated MR 58.81 and 6.8 g of b.p. 171-174° (0.01 mm); n_D^{20} 1.5020; d_0^{20} 1.2313; Found MR 59.02. $C_{10}H_{15}O_5P$. Calculated MR 58.81. Found: P 12.56; 12.35%. $C_{10}H_{15}O_5P$. Calculated: P 12.59%.

On distillation at 0.5 mm: b.p. 176-180°; n_D^{20} 1.4997; d_0^{20} 1.2110. In a repeat experiment, from 11.9 g of p-benzoquinone and 15.2 g of diethyl phosphite we obtained 8 g of a substance of b.p. 169-170° (0.02 mm); n_D^{20} 1.5036; d_0^{20} 1.2156; Found MR 59.917. $C_{10}H_{15}O_5P$. Calculated MR 58.81. Found: P 12.64; 12.57%. Calculated: P 12.59%.

Hydrolysis of the product. The substance (2.3 g) was refluxed for 24 hours with dilute (1 : 1) hydrochloric acid (25 ml). After removal of water under reduced pressure we isolated 1.2 g of hydroquinone, m.p. 169-170°; a mixture test showed m.p. 169-170°. From the liquid part we obtained phenylhydrazine phosphate by treatment with phenylhydrazine. Melting point after recrystallization 158-159°; a mixture test showed 158-159°.

Acetylation of the product. To 4 g of diethyl p-hydroxyphenyl phosphate we added 2.9 g (2 moles per mole of ester) of freshly distillated acetyl chloride; some heat was evolved. The mixture was heated for one hour in a water bath at about 50°, and then one hour further in a boiling water bath. The resulting thick colorless liquid

was subjected to molecular distillation and was then distilled in a high vacuum from an Arbuzov flask. At first crystals appeared in the distillate in addition to liquid (hydroquinone diacetate, m.p. 120-121°). We obtained 1.5 g of p-acetoxyphenyl diethyl phosphate; b.p. 113-115° (0.035 mm); n_D^{20} 1.4841; d_{20}^{20} 1.2049; Found MR 68.67. $C_{12}H_{17}O_6P$. Calculated MR 68.17. Found: P 10.81; 11.15%. Calculated: P 10.76%.

p-Acetoxyphenyl diethyl phosphate (0.4 g) was boiled with dilute (1 : 1) hydrochloric acid (10 ml). After repeated evaporation on a water bath, a solid residue was isolated. Because of the small amounts obtained, hydroquinone was identified as quinhydrone. We obtained black crystals, m.p. 168-170°. The literature gives m.p. 171°. From the liquid part we prepared phenylhydrazine phosphate, m.p. 157.5-158°; a mixture test showed m.p. 158°.

Reaction of Hydroquinone with Diethyl Phosphorochloridate. Triethylamine (14.5 g) was added to a solution of 16 g of hydroquinone in 200 ml of dry ether. There was a rise in temperature, and a precipitate formed. On addition of 25 g of diethyl phosphorochloridate, some heat was evolved and the precipitate changed in character. The solution became bluish violet. The contents of the flask were heated in a water bath for 2.5 hours. The precipitate of triethylamine hydrochloride was filtered off (18 g). After removal of ether, the residue was distilled in a high vacuum. We obtained the following fractions: I) b.p. 148-157° (0.01 mm); n_D^{20} 1.4981; d_0^{20} 1.2176; Found MR 59.29. $C_{10}H_{15}O_5P$. Calculated MR 58.81. Found: P 12.14; 12.06%. Calculated: P 12.59%. II) b.p. 156-159° (0.01 mm); n_D^{20} 1.4857; d_0^{20} 1.2180; Found MR 58.01. $C_{10}H_{15}O_5P$. Calculated MR 58.81. Found: P 14.36; 14.75%. Calculated: P 12.59%.

Hydrolysis. The fraction of b.p. 148-157° (0.01 mm) (5 g) was hydrolyzed by boiling it with dilute (1 : 1) hydrochloric acid. We obtained 2.4 g of hydroquinone, m.p. 170-171°. On addition of phenylhydrazine to the residue obtained after repeated evaporation of the filtrate we obtained phenylhydrazine phosphate, m.p. 159-160°.

Acetylation. The fraction of b.p. 148-157° (0.01 mm) (2 g) was heated on a water bath for 90 minutes with acetyl chloride (1.8 g), and the system was then connected to the vacuum of a water pump and heating was continued for one hour. On cooling, the contents of the flask crystallized. After separation from a small amount of liquid part the crystals were recrystallized from alcohol and were found to be hydroquinone diacetate (m.p. 119-120°). The liquid part could not be distilled.

Reaction of 1,4-Naphthoquinone with Diethyl Phosphite. 1,4-Naphthoquinone (8.7 g) and diethyl phosphite (7.5 g) were dissolved in 20 ml of dioxane, and 25 drops of a saturated solution of sodium ethoxide were added. The addition of the first 5-7 drops resulted in rise of temperature to 75-80°. Further additions caused no further rise. At the end the contents of the flask were heated in a water bath at 80° for 30 minutes. On cooling, 1 ml of acetic acid was added and the contents of the flask were poured into water. The dark-brown layer gradually crystallized out with formation of brown grains. After separation, washing with water, and two crystallizations from ether, we obtained pale-pink crystals, m.p. 99-101.5°. After recrystallization from ether with the addition of animal charcoal we obtained well-defined colorless crystals, m.p. 101-102°. Found: P 10.59; 10.63%. $C_{14}H_{17}O_5P$. Calculated: P 10.47%. With ferric chloride an alcoholic solution of the substance gave a cherry-red color, which passed into lilac.

Hydrolysis of the product of m.p. 101-102°. The substance (1.5 g) was heated for eight hours with dilute (1 : 1) hydrochloric acid (20 ml). After crystallization from water the resulting flocculent precipitate had m.p. 177-179°, undepressed by admixture of 1,4-naphthalenediol. From the aqueous part, after evaporation and treatment with phenylhydrazine, we obtained phenylhydrazine phosphate, m.p. 154-155°.

Preparation of the acetic ester. To 1.2 g of the product of m.p. 101-102° we added 0.8 g of acetyl chloride. The flask was heated in a water bath for 20 minutes. Distillation gave 0.9 g of substance having b.p. 199-202° (0.3 mm); n_D^{20} 1.5383; d_0^{20} 1.2277; Found MR 86.24. $C_{16}H_{19}O_6P$. Calculated MR 86.33.* Calculated: P 9.14%. Found: P 9.44; 9.53%.

Hydrolysis of the monoacetic ester. The substance (1.1 g) was boiled with dilute (1 : 1) hydrochloric acid (20 ml) for two hours; the flocculent precipitate was recrystallized from water and then had m.p. 181-183°. A mixture with 1, 4-naphthalenediol had m.p. 181-183°. From the aqueous layer, with the aid of phenylhydrazine, we obtained phenylhydrazine phosphate, m.p. 153-154°.

*Exaltation due to naphthalene ring: 2.82.

SUMMARY

The addition of diphenyl phosphite to p-benzoquinone and to 1,4-naphthoquinone in presence of sodium alkoxide led to the formation of diethyl p-hydroxyphenyl phosphate and diethyl 4-hydroxy-1-naphthyl phosphate, respectively.

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SYNTHESIS OF ORGANOSILICON COMPOUNDS FROM p-DIBROMOBENZENE

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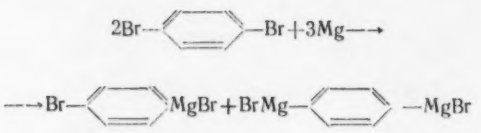
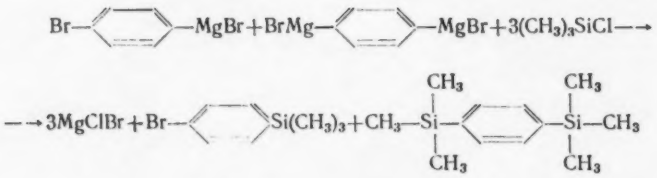
In the previous communication [1] we described the synthesis of linear compounds having phenylenesiloxane chains in the molecule. In the present work we have carried out syntheses from p-dibromobenzene with the object of obtaining and further transforming organosilicon compounds containing the p-bromophenyl group.

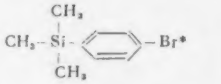
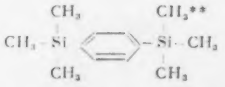
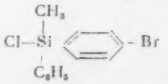
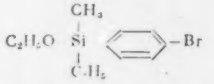
In the study of the reaction of p-dibromobenzene with magnesium and chlorotrimethylsilane and also dichloromethylphenylsilane we isolated new compounds, whose properties are given in the table. The reaction of p-dibromobenzene, magnesium, and chlorotrimethylsilane leads, as our experiments showed, to the formation of p-bromophenylmagnesium bromide and p-phenylenebis [magnesium bromide] in accordance with the scheme:



This is confirmed by the fact that in the decomposition of magnesium derivatives of p-dibromobenzene with chlorotrimethylsilane there is simultaneous formation of p-bromophenyltrimethylsilane and p-bistrimethylsilylbenzene:



The latter is a crystalline solid, whereas the p-bistrimethylsilylbenzene described in the literature [2] is a liquid. Judging by the yields of p-bromophenyltrimethylsilane and p-bistrimethylsilylbenzene, the formation of p-phenylenebis [magnesium bromide] proceeds at a considerably lower rate than that of p-bromophenylmagnesium bromide, for the yield of p-bistrimethylsilylbenzene was 11.8% and that of p-bromophenyltrimethylsilane was 52%. The over-all yield of the two compounds was 63.8%.

Compound	Formula	B.p. in °C (p in mm)	M.p.(°C)	d_4^{20}	n_D^{20}	MR found	MR calc.
p-Bromophenyltrimethylsilane		69 (1) 100 (10)	—	1,2219	1,5309	58,01	58,02
1,4-Bistrimethylsilylbenzene		194 (742)	95,5—96,5	—	—	—	—
p-Bromophenylchloromethylphenylsilane		130—131 (1)	—	1,3575	1,5650	78,02	77,71
p-Bromophenylethoxymethylphenylsilane		145 (1)	—	1,2626	1,5706	83,57	83,58

* The literature [3] gives: b.p. 146-148° (50 mm); d_4^{20} 1.2197; n_D^{20} 1.5302.

** The literature [4] gives: b.p. 143° (43 mm); m.p. 88°.

On the decomposition of the organomagnesium compounds obtained from p-dibromobenzene and magnesium with dichloromethylphenylsilane, we isolated p-bromophenylchloromethylphenylsilane in 25.8% yield. It is interesting that the chlorine in p-bromophenylchloromethylphenylsilane is replaced to the extent of 92% by alkoxyl when the compound is heated with alcohol at a temperature of not above 78°.

EXPERIMENTAL

Preparation of p-Bromophenyltrimethylsilane. One mole (109 g) of chlorotrimethylsilane (chlorine content 32.7%; the calculated value is 32.36%) was added in presence of a small crystal of iodine to Br—C$_6$H$_4$—MgBr, prepared from one gram-atom (24.3 g) of magnesium and one mole (236 g) of p-dibromobenzene (m.p. 87.8°) in one liter of ether. The mixture was boiled for seven hours at 36-41°, and the solid magnesium derivatives were washed with ether. The ether layer was separated and fractionated. We obtained 119.2 g (52%) of a substance of b.p. 69° (1 mm) [100° (10 mm)], which corresponded to p-bromophenyltrimethylsilane, and 13.1 g (11.8%) of a substance of b.p. 194° and m.p. 95.5-96.5° (from absolute ethanol), which corresponded to p-bistrimethylsilylbenzene. p-Bistrimethylsilylbenzene is a white crystalline substance which readily crystallizes from absolute ethanol (1 g of substance, 5 ml of alcohol) and is soluble in diethyl ether, benzene, chlorobenzene, petroleum ether, acetone, carbon tetrachloride, methanol, and ethanol. It is insoluble in water. It sublimes at 80-81°. Found: C 47.30; 47.53; H 5.90; 5.92; Si 11.90; 12.10; Br 34.94; 34.98%. $C_9H_{13}SiBr$. Calculated: C 47.16; H 5.72; Si 12.26; Br 34.86%. Found: mol. wt. 223.223; calculated mol. wt. 229.2. Found: C 64.87; 64.76; H 10.05; 10.14; Si 25.13; 25.04%. $C_{12}H_{22}Si_2$. Calculated: C 64.78; H 9.97; Si 25.25. Found mol. wt. 222.219; calculated mol. wt. 222.5.

Preparation of p-Bromophenylchloromethylphenylsilane. One mole (192 g) of dichloromethylphenylsilane (chlorine content 37.9%; the calculated value is 37.1%) was added in presence of a small crystal of iodine to Br—C$_6$H$_4$—MgBr prepared from one gram-atom (24.3 g) of magnesium and one mole (236 g) of p-dibromobenzene in one liter of ether. The mixture was boiled at 36-41° for six hours, and the solid magnesium derivatives were washed with ether. The ether layer was separated and vacuum-fractionated. We obtained 80.5 g (25.8%) of a substance of b.p. 130-131° (1 mm), corresponding to p-bromophenylchloromethylphenylsilane. Found: C 49.99; 50.21; H 4.19; 4.21; Si 9.14; 9.34; Cl 11.20; 11.51; Br 25.24; 25.83%. $C_{13}H_{12}SiClBr$. Calculated: C 50.09; H 3.88; Si 9.01; Cl 11.38; Br 25.64%. Found mol. wt. 318; calculated mol. wt. 311.7.

Preparation of p-Bromophenylethoxymethylphenylsilane. Over a period of 45 minutes 9.4 g of p-bromophenylchloromethylphenylsilane was added to 2.00 g (30% excess) of absolute ethanol at 24-26°. The contents of the flask were heated with stirring at 71-78° for 12 hours. Vacuum fractionation of the mixture gave 8.92 g (92%) of a substance of b.p. 145° (1 mm), corresponding to p-bromophenylethoxymethylphenylsilane. Found: C 56.29; 55.92; H 5.51; 5.67%. $C_{15}H_{17}SiOBr$. Calculated: C 56.07; H 5.34%. Found mol. wt. 321; calculated mol. wt. 321.3.

SUMMARY

1. The reaction of magnesium with p-dibromobenzene and chlorotrimethylsilane was investigated and it was shown that there is simultaneous formation of p-bromophenyltrimethylsilane and p-bistrimethylsilylbenzene in the proportions of 4.4 : 1.

2. The new compounds, p-bromophenylchloromethylphenylsilane and p-bromophenylethoxymethylphenylsilane, were synthesized.

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FLUORINE-CONTAINING β-SULTONES

COMMUNICATION 3. REACTION OF FLUORINE-CONTAINING β-SULTONES WITH ALCOHOLS

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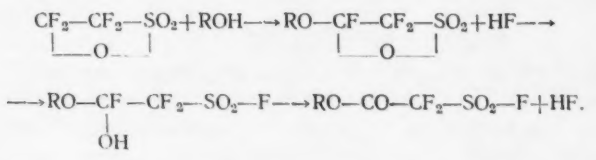
In the previous investigation [1] we examined the hydrolysis of tetrafluoro-2-hydroxyethanesulfonic acid β-sultone, which was prepared by the addition of sulfur trioxide to tetrafluoroethylene [2]. It was shown that treatment of this sultone with an equimolecular amount of water resulted in the quantitative formation of difluoro (fluorosulfonyl) acetic acid. In view of this it may be supposed that treatment of fluorine-containing β-sultones with alcohols would result in the formation of esters of the corresponding (fluorosulfonyl) carboxylic acids. Actually, on addition of alcohols to tetrafluoro-2-hydroxyethanesulfonic acid β-sultone there was a considerable evolution of heat and liberation of hydrogen fluoride; moreover, these visible signs of reaction were to be observed only during the addition of the first molecular proportion of alcohol. After washing the reaction mixture with water and fractionation, we obtained a quantitative yield of the difluoro (fluorosulfonyl) acetic ester. The methyl, ethyl, and isopropyl esters isolated in this way were completely identical with the compounds obtained previously from difluoro (fluorosulfonyl) acetic acid and the corresponding alcohols [1]. Similarly, by the reaction of other fluorine-containing β-sultones with alcohols we obtained the methyl and ethyl esters of fluoro (fluorosulfonyl) acetic acids and the methyl ester of tetrafluoro-2-(fluorosulfonyl) propionic acid.

It is known [3] that on methanolysis of the mixture obtained by treatment of styrene with a solution of dioxane-sulfur trioxide in dichloroethane, 2-methoxy-2-phenylethanesulfonic acid is formed. On the basis of this fact it was suggested that in the first stage of the reaction of hypothetical hydrogen-containing β-sultones with alcohols the cleavage of the lactone ring occurs. However, in the case of fluorine-containing β-sultones the reaction undoubtedly proceeds differently. In fact, if in the first stage of the reaction the cleavage of a lactone ring occurred, then the β-fluoro β-alkoxy sulfonic acid would react with the excess of alcohol, which is not in accord with observation. It may be supposed that reaction begins with the replacement of a β-fluoro by alkoxyl; then the hydrogen fluoride liberated opens the lactone ring of the β-alkoxy β-sultone; and finally hydrogen fluoride is eliminated from the β-alkoxy β-fluoro β-hydroxy compound:



On the other hand it may be supposed that under alcoholysis conditions the original cyclic β-sultone isomerizes into a linear bis (acid fluoride) of a sulfo carboxylic acid, which reacts with the alcohol with formation of a (fluorosulfonyl) carboxylic ester:

$$CF_2(-O-)CF_2-SO_2 \longrightarrow F-CO-CF_2-SO_2-F \xrightarrow[-HF]{+ROH} RO-CO-CF_2-SO_2-F$$

The α-(fluorosulfonyl) carboxylic esters liberated are hydrolytically stable substances; they can be steam-distilled without decomposition; even when they are boiled for a long time with water or alcohols there is no cleavage of the fluorosulfonyl bond (fluoride cannot be detected in the solution). However, this cleavage is readily effected by the action of aqueous alkalis or alcoholic solutions of alkali-metal alkoxides. Thus, on treatment of ethyl difluoro (fluorosulfonyl) acetate with alcoholic sodium ethoxide, sodium (ethoxycarbonyl) difluoromethanesulfonate is formed. It is probable that in the first stage of the reaction diethyl difluoro-sulfoacetate is formed, which then alkylates the sodium salt. The over-all reaction is described by the equation:

$$F-SO_2-CF_2-CO-OC_2H_5 + C_2H_5ONa \longrightarrow NaO-SO_2-CF_2-CO-OC_2H_5 + C_2H_5F$$

This reaction is analogous to that proposed for the formation of salts of alkanesulfonic acids [4] and is an indirect confirmation of the presence of a fluorosulfonyl group in the molecule of the original difluoro (fluorosulfonyl) acetic ester.

Sodium (ethoxycarbonyl) difluoromethanesulfonate is converted by solutions of alkali into disodium difluorosulfoacetate, identical with the salt obtained by the neutralization of the hydrolyzate of tetrafluoro-2-hydroxyethanesulfonic acid β-sultone [2].

$$NaO-SO_2-CF_2-CO-OC_2H_5 + NaOH \longrightarrow NaO-SO_2-CF_2-CO-ONa + C_2H_5OH$$

It was unexpected to find that α-(fluorosulfonyl) carboxylic esters are relatively inert toward amines. Thus, ethyl difluoro (fluorosulfonyl) acetate does not react with aniline at room temperature; reaction is observed only when heat is applied. In this case the product of the reaction was found to be the dianilide of difluorosulfoacetic acid:

$$F-SO_2-CF_2-CO-OC_2H_5 + 3C_6H_5-NH_2 \longrightarrow$$
$$\longrightarrow C_6H_5-NH-SO_2-CF_2-CO-NH-C_6H_5 + C_2H_5OH + C_6H_5NH_2 \cdot HF$$

In this case the formation of the intermediate product, i.e., difluoro (fluorosulfonyl) acetanilide, was not observed. This compound was prepared by the action of an ethereal solution of aniline on tetrafluoro-2-hydroxyethanesulfonic acid β-sultone:

$$CF_2(-O-)CF_2-SO_2 + C_6H_5NH_2 \longrightarrow C_6H_5-NH-CO-CF_2-SO_2-F + HF$$

EXPERIMENTAL

Methyl Difluoro (fluorosulfonyl) acetate. At 0-5° 4.6 g of dry methanol was added slowly dropwise to 18.0 g of tetrafluoro-2-hydroxyethanesulfonic acid β-sultone; the temperature rose, and hydrogen fluoride was liberated. The reaction mixture was washed with two 20-ml portions of ice water. The lower, oily layer was separated, dried over anhydrous magnesium sulfate, and fractionated under atmospheric pressure. We isolated 18.0 g (95 %) of methyl difluoro (fluorosulfonyl) acetate; b.p. 115-116°; d_4^{20} 1.5162; n_D^{20} 1.3504. For methyl difluoro (fluorosulfonyl) acetate the literature [1] gives b.p. 115°; d_4^{20} 1.5159; n_D^{20} 1.3510.

Ethyl Difluoro (fluorosulfonyl) acetate. This was prepared similarly from tetrafluoro-2-hydroxyethanesulfonic acid β-sultone and ethanol in 95% yield. The physical properties were identical with those given previously [1].

Isopropyl Difluoro (fluorosulfonyl) acetate. This was prepared similarly from tetrafluoro-2-hydroxyethanesulfonic acid β-sultone and isopropyl alcohol in 93% yield. The physical properties were identical with those given previously [1].

Methyl Fluoro (fluorosulfonyl) acetate. This was prepared similarly from 1,2,2-trifluoro-2-hydroxyethanesulfonic acid β-sultone and methanol in 95% yield; b.p. 172-173°; d_4^{20} 1.5160; n_D^{20} 1.3875. Found: F 22.00; S 18.62%; mol. wt. 175.9; acidity equivalent 3.00. $C_3H_4O_4F_2S$. Calculated: F 21.83; S 18.27%; mol. wt. 174.4; acidity equivalent 3.00.

Ethyl Fluoro (fluorosulfonyl) acetate. This was prepared similarly from 1,2,2,-trifluoro-2-hydroxyethanesulfonic acid β-sultone and ethanol in 94% yield; b.p. 179-180; d_4^{20} 1.3959; n_D^{20} 1.3880. Found: F 19.64; S 17.27; mol. wt. 186.0; acidity equivalent 2.97. $C_4H_6O_4F_2S$. Calculated: F 20.21; S 17.02%; mol. wt. 188.4; acidity equivalent 3.00.

Methyl Tetrafluoro-2-(fluorosulfonyl) propionate. This was prepared similarly from trifluoro-2-hydroxy-1-(trifluoromethyl) ethanesulfonic acid β-sultone and methanol in 92% yield; b.p. 118-119°; d_4^{20} 1.5600; n_D^{20} 1.3415. Found: C 19.74; H 1.01; F 39.78; S 13.04%; mol. wt. 240.0; acidity equivalent 3.04. $C_4H_3O_4F_5S$. Calculated: C 19.82; H 1.25; F 39.19; S 13.23%; mol. wt. 242.4; acidity equivalent 3.00.

Sodium (Ethoxycarbonyl) difluoromethanesulfonate. A solution of 0.23 g of sodium in 10 ml of dry ethanol was added dropwise to a solution of 2.06 g of ethyl difluoro (fluorosulfonyl) acetate in 10 ml of dry ethanol at such a rate that the reaction temperature did not exceed 45-50°. The separation of a white crystalline precipitate was observed. The reaction mixture was cooled and diluted with 80 ml of dry ether. The precipitate was filtered off and crystallized from 40 ml of an alcohol-ether mixture (1 : 1). We obtained 1.6 g of white needles of sodium (ethoxycarbonyl) difluoromethanesulfonate, m.p. 191-192°, readily soluble in water, somewhat soluble in alcohol, and insoluble in ether. Found: C 20.92; H 2.08; F 16.26; S 14.00%. $C_4H_5O_5F_2SNa$. Calculated: C 21.20; H 2.20; F 16.84; S 14.25%.

Disodium Difluorosulfoacetate. A solution of 1.1 g of sodium (ethoxycarbonyl) difluoromethanesulfonate in 10 ml of water was neutralized to phenolphthalein with 1 N NaOH (about 4.95 ml). The neutralized aqueous solution was evaporated to dryness. The crystalline residue was recrystallized from alcohol and washed with ether. We obtained 0.9 g of white needles of disodium difluorosulfoacetate, which melted above 300°. Found: C 11.25; F 16.95; S 14.35%. $C_2O_5F_2SNa_2$. Calculated: C 10.91; F 17.20; S 14.57%.

Dianilide of Difluorosulfoacetic Acid. A mixture of 4.1 g of ethyl difluoro (fluorosulfonyl) acetate and 5.6 g of freshly distilled aniline was heated in a water bath for two hours. The mixture was then washed with two 20 ml portions of hot water. The viscous oil was left overnight, when it partly crystallized. The crystals were filtered off under suction and recrystallized from 20 ml of 1 : 1 aqueous alcohol. We isolated 4.5 g of white prisms of the dianilide of difluorosulfoacetic acid, m.p. 162-163°, insoluble in water, readily soluble in alcohol and ether. Found: C 51.20; H 3.51; N 8.61; F 11.55; S 10.07%; mol. wt. 319.5. $C_{14}H_{12}O_3N_2F_2S$. Calculated: C 51.52; H 3.70; N 8.58; F 11.65; S 9.83%; mol. wt. 326.5.

Difluoro (fluorosulfonyl) acetanilide. A solution of 2.3 g of freshly distilled aniline in 20 ml of dry ether was added slowly dropwise with ice cooling to a solution of 4.5 g of tetrafluoro-2-hydroxyethanesulfonic acid β-sultone in 20 ml of dry ether. The mixture became warm and hydrogen fluoride was evolved; the solution turned yellow. Ether was removed in a vacuum, and the residue (a thick yellow oil) crystallized on standing. Recrystallization from petroleum ether (b.p. 50-60°) gave 4.5 g of white needles of difluoro (fluorosulfonyl) acetanilide, m.p. 104-105°, insoluble in water, readily soluble in alcohol, ether, and benzene; yellows on standing. Found: C 38.24; H 2.60; N 5.32; F 21.84%; mol. wt. 260.7. $C_7H_6O_3NF_3S$. Calculated: C 37.92; H 2.37; N 5.55; F 22.10%; mol. wt. 253.4.

SUMMARY

1. Fluorinated α-(fluorosulfonyl) carboxylic esters were prepared by the alcoholysis of fluorine-containing β-sultones.

2. The action of sodium alkoxide and of aniline on ethyl difluoro (fluorosulfonyl) acetate was studied.

3. Difluoro (fluorosulfonyl) acetanilide was prepared by the action of aniline on tetrafluoro-2-hydroxy-ethanesulfonic acid β-sultone.

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*Original Russian pagination. See C. B. translation.

FLUORINE-CONTAINING β-SULTONES

COMMUNICATION 4. PREPARATION OF TETRAFLUORO-2-HYDROXY-ETHANESULFONIC ACID β-PYROSULTONE

G. A. Sokol'skii, M. A. Dmitriev, and I. L. Knunyants

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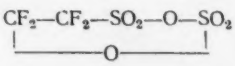
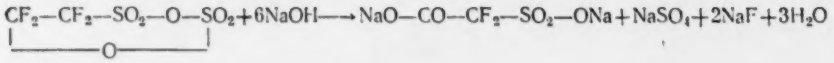
It was earlier reported [1] that by the reaction of the α-modification of sulfur trioxide with fluoro olefins, four-membered ring compounds, namely fluorine-containing β-sultones, are formed in almost quantitative yield. It was observed that a small amount of higher-boiling fluorine-containing products was formed at the same time. Thus, in the reaction of tetrafluoroethylene with sulfur trioxide stabilized by the addition of 10% of dimethyl sulfate, after the isolation of the main reaction product (tetrafluoro-2-hydroxyethanesulfonic acid β-sultone, b.p. 32-33°) there remained a somewhat viscous dark-colored liquid, which contained fluorine and sulfur and partly distilled over above 100°.

It was found that the formation of by-products in the reaction of the α-modification of sulfur trioxide with tetrafluoroethylene is not associated with any transformation of the main reaction product, tetrafluoro-2-hydroxyethanesulfonic acid β-sultone. This was shown by the following experiments. When an equimolecular mixture of sulfur trioxide and tetrafluoro-2-hydroxyethanesulfonic acid β-sultone was heated in an autoclave for two hours at 60-70°, a fraction was separated which distilled over the range 32-50° and corresponded in amount to the sum of the amounts of starting materials taken; higher-boiling fluorine-containing fractions were quite absent from the reaction mixture. Neither was the formation of any reaction products observed when an equimolecular mixture of tetrafluoro-2-hydroxyethanesulfonic acid β-sultone and the other starting compound, i.e., tetrafluoroethylene, was heated in an autoclave for two hours at 60-70°; the two substances were recovered unchanged quantitatively. When this mixture was heated in an autoclave at 150-160° the β-sultone was again isolated quantitatively, but the tetrafluoroethylene was converted into a white amorphous powder, which appeared to be a polymerization product of the Teflon type. Again, no reaction products were formed when tetrafluoro-2-hydroxyethanesulfonic acid β-sultone was heated with the stabilizer for sulfur trioxide, i.e., dimethyl sulfate.

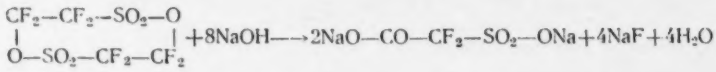
We succeeded in isolating the by-products of the reaction of the α-modification of sulfur trioxide with tetrafluoroethylene directly from the reaction mixture after the removal of tetrafluoro-2-hydroxyethanesulfonic acid β-sultone by distillation. By the fractionation of ten portions of the residue we isolated two by-products of the reaction and unchanged stabilizer, dimethyl sulfate. It was found that one of the by-products, which comprised the major portion of the residue, was the product of the addition of two molecules of sulfur trioxide to one molecule of tetrafluoroethylene, i.e,, tetrafluoro-2-hydroxyethanesulfonic acid β-pyrosultone:



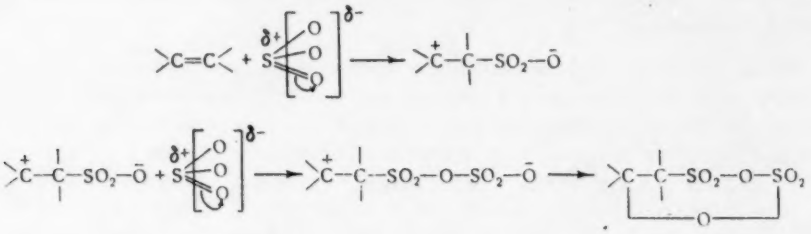
The structure of this compound was proved by the fact that in the treatment of a weighed sample of the preparation with aqueous alkali exactly six equivalents of alkali were consumed and two equivalents of fluoride ion were to be found in the solution:



The second by-product of the reaction was found to be the product of the combination of two molecules of tetrafluoroethylene and two molecules of sulfur trioxide. On the basis of the fact that on treatment of a weighed sample of this substance with aqueous alkali eight equivalents of alkali were consumed and four equivalents of fluoride ion were found in the solution it must be supposed that this compound is the cyclic dimer of the main reaction product (tetrafluoro-2-hydroxyethanesulfonic acid β-sultone).

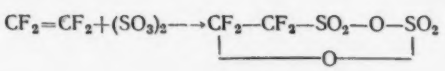


The possibility of the existence of β-pyrosultones, which are anhydrides of substituted ethionic acids and have been generally referred to in the literature as "carbyl sulfates", was indicated long before their isolation from the products of the sulfonation of olefins [2]. The isolation of salts of substituted ethionic acids from the hydrolyzate obtained after reaction of an olefin with oleum or with a solution of dioxane-sulfur trioxide has been cited in proof of the formation of pyrosultones. Finally, in individual cases hydrogen-containing β-pyrosultones have been isolated; e.g., in the reaction of ethylene with sulfur trioxide [3], and of 2-(chloromethyl) propene and of 1-hexene with excess of dioxane-sulfur trioxide [4]. It is considered that β-pyrosultones are formed by the addition of a second sulfur trioxide molecule to the originally formed dipole [5]:



If the view, advanced previously [1], of the ionic character of the reaction of tetrafluoroethylene with sulfur trioxide is correct, then the above scheme explains the formation of tetrafluoro-2-hydroxyethanesulfonic acid β-sultones as one of the by-products of the reaction. On the same basis we may explain also the formation of the other by-product of the reaction, i.e., the cyclic dimer of tetrafluoro-2-hydroxyethanesulfonic acid β-sultone, namely on the basis of the intermolecular association of two dipoles.

The formation of tetrafluoro-2-hydroxyethanesulfonic acid β-pyrosultone may be associated also with the presence of a certain amount of the dimeric form of sulfur trioxide in the sulfur trioxide used in the reaction. This view is based on the fact that, as we have shown, tetrafluoro-2-hydroxyethanesulfonic acid β-pyrosultone is the main reaction product when a mixture of tetrafluoroethylene and the β-modification of sulfur trioxide (the dimer) is heated in an autoclave in absence of stabilizer:



It was found that in this reaction tetrafluoro-2-hydroxyethanesulfonic acid β-sultone was a by-product.

EXPERIMENTAL

Tetrafluoro-2-hydroxyethanesulfonic Acid β-Sultone and Sulfur Trioxide. A 100 ml steel autoclave was charged successively with 8.0 g of freshly distilled sulfur trioxide (stabilized with 0.8 g of dimethyl sulfate) and 18.0 g of tetrafluoro-2-hydroxyethanesulfonic acid β-sultone. The autoclave was hermetically closed and heated for two hours at 60-70°. When cool, the autoclave was opened and the contents were distilled at amospheric pressure. We collected a fraction of b.p. 32-50° (25.5 g). From the residue (1.1 g of a light-brown liquid) distillation under reduced pressure gave 0.6 g of dimethyl sulfate.

Tetrafluoro-2-hydroxyethanesulfonic Acid β-Sultone and Tetrafluoroethylene. a) A 100 ml steel autoclave cooled to -100° was charged successively with 18.0 g of the β-sultone and 10.0 g of tetrafluoroethylene. The autoclave was hermetically closed and was gradually heated: up to room temperature in the course of two hours, and then for two hours at 60-70°. The autoclave was cooled to -100° and opened; the gaseous products were driven off and condensed in a trap at -100° as a colorless liquid (9.5 g), which was found to be tetrafluoroethylene. The residue distilled off completely from a water bath and 17.5 g of tetrafluoro-2-hydroxyethanesulfonic acid β-sultone was collected.

b) The same mixture of starting materials was heated in an autoclave at 150-160° for two hours. The autoclave was cooled to -100° and opened; 17.4 g of the β-sultone was distilled from the contents. The solid residue was washed with three 50 ml portions of water, and was then washed with alcohol and ether; it was a white amorphous powder, inert toward concentrated alkalis and to sulfuric and nitric acids; it consisted of polytetrafluoroethylene. Found: C 23.56; F 75.24; S 0.00%. CF_2. Calculated: C 24.00%. F 76.00%.

Tetrafluoro-2-hydroxyethanesulfonic Acid β-Sultone and Dimethyl Sulfate. A 100 ml steel autoclave was charged successively with 12.6 g of dimethyl sulfate and 18.0 g of the β-sultone. The autoclave was hermetically closed and heated for two hours at 60-70°. When cool, the autoclave was opened, and the contents were fractionated, first at atmospheric and then at reduced pressure. We isolated 17.4 g of the β-sultone and 11.5 g of dimethyl sulfate.

Fractionation of the Residue from the Reaction Mixture Obtained from Tetrafluoroethylene and the α-Modification of Sulfur Trioxide [1]. Ten portions of residue from the reaction mixture obtained from tetrafluoroethylene and sulfur trioxide (stabilized with dimethyl sulfate) after the removal of tetrafluoro-2-hydroxyethanesulfonic acid β-sultone (163.4 g) were combined (23.2 g) and fractionated, first at atmospheric and then at reduced pressure. We obtained the following fractions: Fraction I of b.p. 105-106°, 11.0 g; Fraction II of b.p. 68-70° (129 mm), 2.5 g; Fraction III of b.p. 110-120° (129 mm), 0.6 g; Fraction IV of b.p. 98-100° (29 mm), 7.4 g; residue (black viscous mass), 2.3 g.

Fraction I was a colorless mobile liquid having d_4^{20} 1.7407 and n_D^{20} 1.3470; it was tetrafluoro-2-hydroxyethanesulfonic acid β-pyrosultone. Found: C 9.40; F 30.04; S 24.75%; mol. wt. 256.0; acidity equivalent 6.06; equivalent of hydrolyzable fluorine 2.02. $C_2O_6F_4S_2$. Calculated: C 9.23; F 29.20; S 24.60%; mol. wt. 260.2.

Fraction II was a colorless liquid having d_4^{20} 1.7625 and n_D^{20} 1.3460; it was the cyclic dimer of tetrafluoro-2-hydroxyethanesulfonic acid β-sultone. Found: C 13.65; F 41.88; S 18.00%; mol. wt. 356.6; acidity equivalent 7.92; equivalent of hydrolyzable fluorine 4.06. $C_4O_6F_8S_2$. Calculated: C 13.33; F 42.22; S 17.78%; mol. wt. 360.4.

Fraction III was a heavy colorless liquid having d_4^{20} 1.7571 and n_D^{20} 1.3470; it was not investigated in greater detail. Fraction IV was a colorless liquid having d_4^{20} 1.3312 and n_D^{20} 1.3870; it was dimethyl sulfate. For dimethyl sulfate the literature gives b.p. 96-98° (27 mm); d_4^{20} 1.33; n_D^{20} 1.3874.

Tetrafluoro-2-hydroxyethanesulfonic Acid β-Pyrosultone. A 100 ml steel autoclave cooled to -100° was charged successively with 16.0 g of crystalline sulfur trioxide (m.p. 43-44.5°) and 10.0 g of tetrafluoroethylene. The autoclave was hermetically closed and gradually warmed: to 0-10° over a period of two hours, and then to 60° over two hours. The autoclave was cooled to -100° and opened; the contents (26.0 g) formed a light-brown liquid, which fumed slightly in air. Two fractionations at atmospheric pressure gave the following fractions: tetrafluoro-2-hydroxyethanesulfonic acid β-sultone (1.8 g); tetrafluoro-hydroxyethanesulfonic acid β-pyrosultone (20.8 g, i.e., 80% yield); resinous residue (3.0 g).

Tetrafluoro-2-hydroxyethanesulfonic acid β-pyrosultone is a colorless mobile liquid, which fumes slightly in air and etches glass; it is readily soluble in benzene, chloroform, and carbon tetrachloride; it reacts with water, alcohols, acids, and amines.

SUMMARY

1. An investigation was made of the by-products of the reaction between tetrafluoroethylene and the α-modification of sulfur trioxide; tetrafluoro-2-hydroxyethanesulfonic acid β-pyrosultone and the cyclic dimer of tetrafluoro-2-hydroxyethanesulfonic acid β-sultone were isolated.

2. By the reaction of tetrafluoroethylene with the β-modification of sulfur trioxide, tetrafluoro-2-hydroxyethanesulfonic acid β-pyrosultone was prepared.

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STEREOCHEMISTRY OF ADDITIONS TO TRIPLE BONDS

COMMUNICATION 7. STEREOCHEMISTRY OF THE HYDROBROMINATION OF BROMOACETYLENES UNDER FREE-RADICAL CONDITIONS

L. D. Bergel'son

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Academy of Sciences of the USSR
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Otdelenie Khimicheskikh Nauk, No. 7, pp. 1235-1240,
July, 1960
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In a previous communication [1] it was shown that under the conditions of photochemical reaction bromine adds to disubstituted acetylenes in a way different from that in which it adds to their ethylene analogs: whereas the bromination of the double bond went selectively by the trans scheme, acetylenes gave considerable amounts of cis-bromination products. It was of interest to compare steric orientations in free-radical additions to acetylenes and olefins in the case of other reagents, in particular hydrogen bromide.

Several cases have been described in the literature in which the free-radical addition of hydrogen bromide to an ethylenic bond proceeds stereospecifically in accordance with the trans-addition scheme: thus, 1-methyl-, 1-chloro-, and 1-bromo-cyclohexenes react with hydrogen bromide with almost quantitative formation of the corresponding cis-1,2-substituted cyclohexanes [2, 3]. Under free-radical conditions trans-2-bromo-2-butene is converted into racemic 2,3-dibromobutane, and from cis-2-bromo-2-butene the meso-dibromide is obtained exclusively [4].

The stereochemistry of the addition of hydrogen bromide to acetylenes has not yet been studied systematically. The results obtained by Smirnov-Zamkov and Shilov [5] in a study of the hydrobromination of diethyl acetylenedicarboxylate show that under the conditions for ionic reaction (e.g., in acetic acid in presence of lithium bromide), and also in a benzene medium, mainly trans addition of the elements of hydrogen bromide occurs; in hexane a mixture of stereoisomers is formed.

In the present communication we describe the results of a study of steric orientation in the free-radical addition of hydrogen bromide to 1-bromoacetylenes:

$$RC{\equiv}CBr + HBr \longrightarrow RCBr{=}CHBr.$$

The reaction was carried out with an excess of the bromoacetylene at -70° under the radiation of a quartz mercury lamp in absence of solvent (i.e., in liquid hydrogen bromide) or in a pentane medium. The dibromides formed in the reaction were identified by comparing their constants and infrared spectra* with the constants and spectra of the corresponding substituted cis- and trans-1,2-dibromoethylenes, which have been described by us previously [6]. Our results are shown in the table.

*Infrared spectra were determined by B. V. Lopatin.

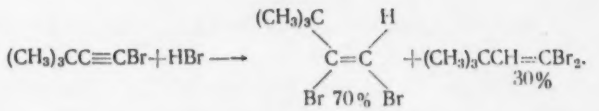
We have previously shown that trans-1,2-dibromo-3,3-dimethyl-1-butene passes almost quantitatively into its cis isomer under ultraviolet radiation at room temperature, whereas trans-1,2-dibromopropene gives a mixture of cis and trans forms in the proportions of 2 : 3 [6]. It is therefore probable that the trans-dibromoethylenes formed in the free-radical hydrobromination of bromoacetylenes at -70° arose not as a result of isomerization, but as primary products of the reaction.

A special experiment in which cis-1,2-dibromo-3,3-dimethyl-1-butene was irradiated for 20 minutes at -70° in presence of HBr did in fact show that under the conditions of hydrobromination the cis-dibromide is not isomerized. On the other hand, under the same conditions pure trans-dibromopropene was converted to the extent of about 20% into the cis isomer. It is therefore probable that the mixture of stereoisomers obtained in the hydrobromination of 1-bromopropyne is formed as a result of the isomerization of the trans-dibromopropene, which is the primary reaction product. Hence, under the conditions indicated there is selective cis addition of the elements of hydrogen bromide to the triple bond.

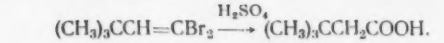
Original bromoacetylene	Trans-cis ratio of 1,2-dibromoethylenes in reaction product	
	in liquid HBr	in pentane
$CH_3 \equiv CBr$	85 : 15*	75 : 15*
$(CH_3)_3CC \equiv CBr$	100% trans	95 : 5

*The product contained some 1,1-dibromopropene (see Experimental).

The free-radical character of the photochemical reaction of hydrobromination is confirmed by the results obtained in the hydrobromination of 1-bromo-3,3-dimethyl-1-butyne with liquid hydrogen bromide in the dark in a nitrogen atmosphere. Under these conditions of ionic hydrobromination, the main product was found to be cis-1,2-dibromo-3,3-dimethyl-1-butene, i.e., the hydrobromination went by the trans-addition scheme. In addition to 1,2-dibromides, about 30% of 1,1-dibromo derivative was formed:

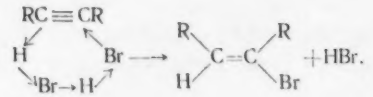


The presence of the latter was confirmed by a study of the infrared spectrum of the reaction product and the formation of 3,3-dimethylbutyric acid on treatment of the mixture of dibromides with concentrated sulfuric acid:



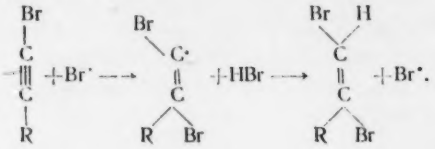
Hence, our results indicate the different steric orientation in free-radical hydrobromination in the 1-bromoethylene and the 1-bromoacetylene series. Whereas in the case of 1-bromoethylenes stereospecific trans addition of hydrogen bromide is observed [2-4], bromoacetylenes give mainly or entirely cis-addition products (trans-dibromides).

In explanation of the cis addition of hydrogen bromide to acetylenedicarboxylic ester Shilov [7] advanced the hypothesis of the formation of a trimolecular complex:

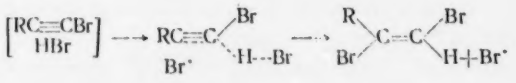


As under the conditions described in the present paper, i.e., in presence of excess of the acetylene compound, the formation of such a complex is not very probable, there remain two possibilities for the explanation of the cis addition of hydrogen bromide:

a) If the addition reaction starts with an attack on the bromine atom [8, 9], then the intermediate radical RCBr = $\dot{C}$Br must be formed. According to Ingold and King [10], whose results indicate that the linear structure for the activated acetylene molecule is energetically unfavorable, such radicals must have an "ethylenelike" configuration. The total (steric and electrostatic) repulsion of two bromine atoms exceeds the repulsion forces between bromine and the alkyl substituent [11, 12]. Hence, the radical formed in the attack of the alkylbromoacetylene by a bromine atom must have the trans configuration. In this case reaction is completed by the cis addition of a hydrogen atom, i.e., the formation of trans-dibromoethylene:

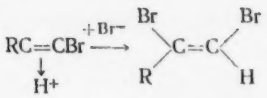


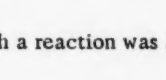
b) If, however, it is assumed that reaction starts with the formation of a complex of the acetylene compound with one molecule of hydrogen bromide, then in some moment of the reaction this complex must have a nonlinear structure:



As a result of the action of electrostatic repulsive forces, the bromine atom approaches the complex from the side opposite to that of the C – Br bond, and the trans-dibromide is formed.

The result of the ionic hydrobromination of 1-bromo-3,3-dimethyl-1-butyne was unexpected: it proceeded structurally nonselectively and differed in orientation from the hydrobromination of 1-bromo-2-alkylethylenes. The nonselectivity of the reaction appears to be the result of the competing effects of the free electron pair of the bromine and the inductive effect of the t-butyl group. It should be noted that in the case of haloacetylenes the π-electrons of the triple bond have, in general, less tendency to interact with the free electron pair of the halogen than in the case of vinyl halides; this is probably due to the lower polarizability of a triple bond, as compared with a double bond [13]. It may therefore be expected that haloacetylenes will be hydrobrominated less selectively under ionic conditions than haloethylenes. The fact that ionic hydrobromination proceeds stereospecifically by the trans-addition scheme indicates that in this case a π-complex is formed:



Actually, if the intermediate product in such a reaction was a carbanion of the type  , it would

be expected that there would be at least a partial attack by the bromide ion from the side opposite to that of the C – Br bond with formation of the trans-dibromo olefin, which is scarcely observed at all.

EXPERIMENTAL

Preparation of 1-Bromopropyne. A solution of potassium hypobromite prepared from 45 g of potassium hydroxide and 16 g of bromine in 300 ml of water at 0° was saturated with propyne while being cooled with ice water. The course of the reaction was followed by iodometric titration of test samples taken from the reaction mixture. After five hours, after the whole of the hypobromite had reacted, the mixture was extracted with ether, and the ether extract was dried with magnesium sulfate and distilled in a nitrogen atmosphere. By fractionation through a column we isolated 14.5 g (61% on the bromine) of 1-bromopropyne; b.p. 64-65° (758 mm); d_4^{25} 1.5230 (determined in a nitrogen atmosphere). We did not succeed in measuring its refractive index because 1-bromopropyne ignites spontaneously in air. In ethereal solution 1-bromopropyne remains unchanged when kept in a refrigerator for one month. According to the literature 1-bromopropyne has b.p. 65°; n_D^{25} 1.4448; d_4^{19} 1.35015 [14] or b.p. 64-65°; d_4^{25} 1.5222 [15]. In the first case [14] the preparation was probably impure.

Preparation of 1-Bromo-3,3-dimethyl-1-butyne. To 300 ml of a 1.2 N solution of potassium hypobromite (prepared from 25 g of bromine, 180 g of potassium hydroxide, 800 ml of water, and 1 g of potassium stearate) containing a few drops of ethanol we added 25 g of 3,3-dimethyl-1-butyne with stirring and cooling with ice water and at such a rate that the temperature of the reaction mixture did not exceed 5°. The mixture was left overnight and stirred further for one hour at 20°, after which the concentration of hypobromite had fallen to 0.15 N. The mixture was extracted with hexane, the extract was dried with magnesium sulfate, and solvent was distilled off at atmospheric pressure with passage of nitrogen. Fractionation gave 34.5 g (69% on the 3,3-dimethyl-1-butyne) of 1-bromo-3,3-dimethyl-1-butyne; b.p. 113° (756 mm); n_D^{20} 1.4515; d_4^{20} 1.216; Found MR 35.69; Calculated MR 35.60. Found: C 45.56; 44.63; H 5.66; 5.95; Br 49.75; 49.87%. C_6H_9Br. Calculated: C 44.74; H 5.63; Br 49.61%.

Free-Radical Hydrobromination of 1-Bromopropyne. a) In pentane. The reaction was carried out with irradiation by means of an immersed PRK-4 quartz mercury lamp (nominal power 200 w) provided with a quartz cooling jacket. Heptane cooled to -180° was pumped through the jacket. The jacketed lamp was lowered straight into the reaction vessel, which was cooled externally with solid carbon dioxide and acetone. A solution of 12 g of 1-bromopropyne (0.1 mole) in 50 ml of pentane was introduced into the reaction vessel, which was fitted with a dropping funnel and a thermometer for the measurement of low temperatures. When the temperature of the solution had fallen to -78°, a solution of dry hydrogen bromide (0.05 mole) in 25 ml of pentane (also cooled to -78°) was added under the radiation of the ultraviolet lamp at such a rate that the temperature of the reaction mixture did not exceed -60°. The mixture was irradiated for 20 minutes at -70°, the radiation was switched off, and the temperature was raised in the dark to 0°. The solution was washed with water and with aqueous sodium bicarbonate solution, and it was dried with magnesium sulfate. Ether and unchanged 1-bromopropyne were distilled off in a stream of nitrogen, and the residue was vacuum-distilled through a column (length 30 cm). We obtained a single fraction of the dibromide (9.2 g; yield 92% on the hydrogen bromide); b.p. 63-65° (61 mm); n_D^{20} 1.5302. Judging from the infrared spectrum (κ_{980} 4.40), the preparation contained 75 ± 7.5% of trans-1,2-dibromopropene, about 15 ± 2% of the cis isomer, and a little 1,1-dibromopropene. Pure trans-1,2-dibromopropene has: b.p. 46-47° (40 mm); n_D^{20} 1.5336; κ_{980} 5.83 [6].

b) Without solvent. A mixture of 12 g of 1-bromopropyne and 4 g of liquid anhydrous hydrogen bromide was irradiated, as indicated above, for 20 minutes at -75°. The temperature was raised in the dark to 0°, when a little unchanged hydrogen bromide was liberated. Fractionation through a column gave 8.3 g of a mixture of dibromopropenes; b.p. 40-44° (30 mm); n_D^{20} 1.5266; judging from the infrared spectrum it contained 45 ± 5% of trans-1,2-dibromopropene. On standing in air the preparation yellowed with the separation of hydrogen bromide, which indicates the presence of 1,1-dibromopropene [16]. For the removal of the latter the mixture of dibromides obtained was stirred for three hours at room temperature with 30 ml of concentrated sulfuric acid, 10 g of ice was added, and the upper layer was separated, washed with water, and dried with calcium chloride. Fractionation gave a single fraction (6.5 g); b.p. 42-43° (30 mm) and n_D^{20} 1.5321; judging from its infrared spectrum it contained 85 ± 10% of trans-1,2-dibromopropene.

Free-Radical Hydrobromination of 1-Bromo-3,3-dimethyl-1-butyne. a) In pentane. The reaction was carried out under the conditions described for 1-bromopropyne. From 16 g of 1-bromo-3,3-dimethyl-1-butyne (0.1 mole) and 4 g of hydrogen bromide (0.05 mole) in 50 ml of pentane, after removal of solvent and unchanged 1-bromo-3,3-dimethyl-1-butyne, we obtained 10.7 g (89% on the hydrogen bromide) of 1,2-dibromo-3,3-dimethyl-1-butene; b.p. 68-70° (16 mm); n_D^{20} 1.5171; judging from the infrared spectrum it contained 95 ± 5% of trans isomer (κ_{980} 0.56) [6].

b) Without solvent. Under the conditions of the free-radical hydrobromination of 1-bromopropyne, from 16 g of 1-bromo-3,3-dimethyl-1-butyne and 4 g of liquid anhydrous hydrogen bromide we obtained 9.1 g (75% on the hydrogen bromide) of 1,2-dibromo-3,3-dimethyl-1-butene; b.p. 68° (16 mm); n_D^{20} 1.5178; the infrared spectrum of this coincided completely with the infrared spectrum of the trans-dibromide described previously [6].

Ionic Hydrobromination of 1-Bromo-3,3-dimethyl-1-butyne. Liquid anhydrous hydrogen bromide (4 g) was added to 1-bromo-3,3-dimethyl-1-butyne containing 0.3 g of diphenylamine in the dark at -70° in a nitrogen atmosphere. The mixture was kept for four hours at -78° and then treated as indicated above. Fractionation through a column gave 10.8 g of a mixture of dibromides of b.p. 51-64° (14 mm) and n_D^{20} 1.5100-1.5160 [the bulk (8.6 g) had n_D^{20} 1.5142]. The infrared spectrum of this product contained the following bands in the 700-2000 cm^{-1} region (intensities are given on a three-grade scale): 1616 (weak), 1580 (strong), 1464 (strong), 1394 (medium), 1370 (strong), 1305 (weak), 1239 (strong), 1196 (strong), 1028 (medium), 980 (very weak), 951 (weak), 943 (strong), 916 (medium), 826 (weak), 805 (strong), 775 (strong), 732 (strong) cm^{-1}. According to these data the substance was a mixture of cis-1,2-dibromo-3,3-dimethyl-1-butene (intense bands at 1580 and 732 cm^{-1} [6]) and the isomeric 1,1-dibromide (absorption bands at 1464, 1370, 1028, and 805 cm^{-1} [17]). Comparison of the intensities of the absorption bands in the region of 1580 cm^{-1} for the mixture of dibromides obtained (κ 0.45) and for the pure cis-dibromide (κ 0.64) [6] shows that the hydrobromination product contained 70 ± 7% of the cis isomer. To separate the isomeric bromides the mixture obtained (10 g) was stirred for three hours at room temperature with 30 ml of concentrated sulfuric acid; the mixture was cautiously diluted with ice and cold water and was extracted with ether. The ether extract was washed with sodium bicarbonate solution until neutral and was dried with calcium chloride. After removal of ether we obtained a single fraction (6.6 g) of b.p. 72-73.5° (16 mm) and n_D^{20} 1.5129; its infrared spectrum was identical with that of pure cis-1,2-dibromo-3,3-dimethyl-1-butene [6]. The alkaline extract was acidified with dilute hydrochloric acid and extracted with ether. After evaporation of the ether extract there remained an oil, which distilled over at 185-190° (temperature of bath) and did not freeze when cooled to -10° (3,3-dimethylbutyric acid melts at 6°). The product (0.6 g) was neutralized to phenolphthalein with 1% NaOH solution and then acidified with two drops of 1% hydrochloric acid; a suspension of 1.4 g of 2-bromo-4'-phenylacetophenone [18] in 30 ml of alcohol was added, and the mixture was boiled for two hours. On standing in a refrigerator there was a precipitate of the p-phenylphenacyl ester of 3,3-dimethylbutyric acid, which melted at 90.0-90.5° after recrystallization from 60% alcohol. The literature [19] gives m.p. 92°. Found: C 77.33; 77.47; H 7.01; 7.08%. $C_{20}H_{22}O_3$. Calculated: C 77.39; H 7.13%.

SUMMARY

The reaction of 1-bromoacetylenes with hydrogen bromide under free-radical conditions occurs mainly according to the cis-addition scheme with formation of substituted trans-dibromoethylenes.

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CHEMISTRY OF 1,3-CYCLOHEXANEDIONE

COMMUNICATION 4. SYNTHESIS AND BACTERIOSTATIC ACTIVITY OF 1,3-CYCLOHEXANEDIONE DERIVATIVES CONTAINING LONG ALIPHATIC CHAINS

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July, 1960
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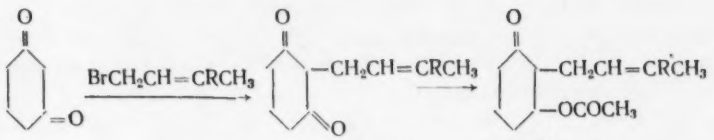
In the preceding investigation [1] we carried out the alkylation of 1,3-cyclohexanedione (dihydroresorcinol) with branched allyl bromides and so obtained the 2-alkyl derivatives (I), (II), (III), and (IV), the enol acetates of which were found to have antihelminthic acitivity:



(I)—(V) (VI)—(IX)

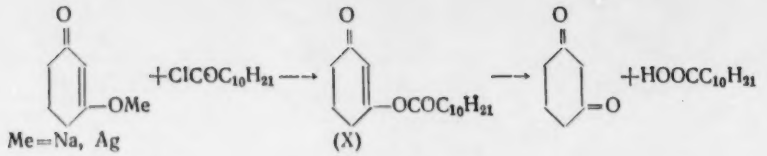
(I) R=CH_3; (IV), (VIII) R=$(CH_2)_3CHCH_3(CH_2)_3CH(CH_3)_2$

(II), (VI) R=$(CH_2)_3CH(CH_3)_2$

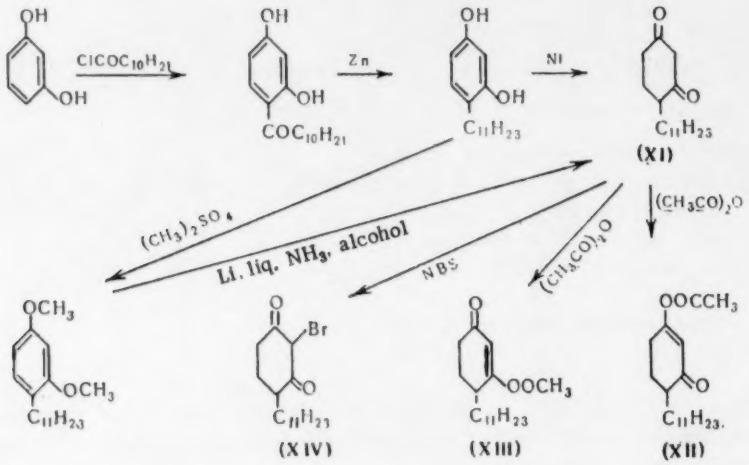
(III), (VII) R=$(CH_2)_2$—CH=$C(CH_3)_2$ (V), (IX) R=C_9H_{19}

In the present communication we describe further investigations on physiologically active 1,3-cyclohexanedione derivatives containing long aliphatic chains. For the synthesis of these compounds we made use not only of C-alkylation, but also of the O-acylation of 1,3-cyclohexanedione with the acid chlorides of higher carboxylic acids and of the hydrogenation of 4-alkylresorcinols, which are readily formed on reduction of the products of the acylation of resorcinol with fatty acids [2]. By the alkylation of 1,3-cyclohexanedione with 1-bromo-3-methyl-2-dodecene in methanol we isolated the corresponding 2-alkyl derivative (V), which when boiled with acetic anhydride gave the enol acetate (IX).

When undecanoyl chloride was heated with the sodium, or better the silver, derivative of 1,3-cyclohexanedione in benzene, as a result of O-acylation we obtained 3-undecanoyloxy-2-cyclohexen-1-one (X), whose structure was confirmed by its alkaline hydrolysis to undecanoic acid and 1,3-cyclohexanedione:



The hydrogenation of 4-undecylresorcinol over Raney nickel in an alkaline medium gave 4-undecyl-1,3-cyclohexanedione (XI), which was obtained in low yield also by the reduction of the dimethyl ether of 4-undecylresorcinol with lithium and liquid ammonia in presence of alcohol. In boiling acetic anhydride 4-undecyl-1,3-cyclohexanedione formed the enol acetate (XII) or (XIII), and under the action of N-bromosuccinimide it gave 2-bromo-4-undecyl-1,3-cyclohexanedione (XIV).



The previously described diketones (I) – (IV) [1] and their enol acetates (VI) – (VIII), and also the newly obtained 1,3-cyclohexanedione derivatives, were tested for bacteriostatic and fungistatic activity in vitro (see table). The preparations (I), (II), (III), and (XI) and 2-bromo-1,3-cyclohexanedione were tested for their behavior toward acid-stable bacteria and molds at dilutions of 1 in 1000 and over and for their behavior toward the other bacteria at dilutions of 1 in 200 and over. The preparations (IV), (VI), VII), (VIII), (X), and (XIV) were tested at dilutions of 1 in 200 and 1 in 400 and over. In view of its instability, (IV) was kept and tested as an alcoholic solution; the dilutions cited are calculated for the pure substance.

As will be seen from the maximum dilutions, cited in the table, at which the growth of microorganisms is retarded, 4-undecyl-1,3-cyclohexanedione (XI), its 2-bromo derivative (XIV), and the diketones (IV) and (V) have high bacteriostatic activity toward human and avian tubercle bacilli. The diketone (IV) and its enol acetate (VIII) have appreciable activity against coccus-type bacteria, and the diketone (IV) and 2-bromo-4-undecyl-1,3-cyclohexanedione show considerable activity toward the acid-stable saprophyte B_5. The simplest 1,3-cyclohexanedione derivatives, namely the enol acetate of 1,3-cyclohexanedione (XV) [3] and 2-bromo-1,3-cyclohexanedione (XVI) [4], have no appreciable bacteriostatic action.

EXPERIMENTAL

2-(3-Methyl-2-dodecenyl)-1,3-cyclohexanedione (V). At -10° 53 g of phosphorus tribromide in 60 ml of isooctane was added to a solution of 105.5 g of 3-methyl-1-dodecen-3-ol [b.p. 125-135° (16 mm); n_D^{20} 1.4385], prepared by the hydrogenation of 3-methyl-1-dodecyn-3-ol [5], in 150 ml of isooctane and 10 ml of pyridine. The solution was warmed to 10°, washed with a dilute sodium bicarbonate solution and with water, dried with magnesium sulfate, and vacuum-evaporated. The resulting bromo compound was used for the alkylation reaction without purification.

Compound	Name of microorganism								
	staph. aureus	strep. hemolyticus	intestinal bac.	typhoid bac.	Flexner dysentery bac.	diphtheria bac. (PW_8)	blue bacillus *	proteus vulgaris	anthracoid spores
(I)	0	0	0	0	0	0	0	0	0
(II)	1 : 8000	1 : 4000	0	0	0	0	0	0	0
(III)	1 : 16 000	1 : 8000	0	0	0	0	0	0	1 : 8000
(IV)	1 : 12 5000	1 : 31 250	0	0	0	1 : 31250	0	0	1 : 31250
(V)	1 : 4000	1 : 4000	0	0	0	0	0	0	0
(VI)	1 : 3200	1 : 1600	0	1 : 800	0	1 : 800	0	0	1 : 800
(VII)	1 : 1600	1 : 800	0	0	0	1 : 1600	0	0	1 : 800
(VIII)	1 : 10 0000	1 : 25 000	0	0	0	1 : 25000	0	0	0
(IX)	1 : 3000	1 : 1600	0	0	0	0	0	0	0
(X)	0	0	0	0	0	0	0	0	0
(XI)	0	0	0	0	0	1 : 4000	0	0	0
(XIV)	1 : 4000	1 : 2000	0	0	0	0	0	0	0
(XV)	1 : 800	1 : 800	1 : 800	1 : 800	1 : 800	1 : 800	1 : 800	1 : 800	1 : 800
(XVI)	0	0	0	0	0	0	0	0	0

Compound	Name of microorganism							
	human tubercle bac.	avian tubercle bac.	acid-stable saprophyte B_5	microsporum	trichophyton	achorion	actinomycete	candida albicans
(I)	1 : 2000	1 : 1000	1 : 1000	1 : 1000	0	1 : 1000	1 : 8000	0
(II)	1 : 16000	1 : 16000	1 : 8000	1 : 1000	1 : 1000	1 : 1000	1 : 1000	0
(III)	1 : 32000	1 : 32000	1 : 16000	1 : 1000	1 : 1000	1 : 2000	1 : 16000	0
(IV)	1 : 2 000 000	1 : 2000000	1 : 1000000	0	0	0	1 : 4000	0
(V)	1 : 2 000 000	1 : 60000	1 : 8000	—	—	—	—	—
(VI)	1 : 25 000	1 : 25000	1 : 400	1 : 3200	1 : 1600	1 : 6400	1 : 800	0
(VII)	1 : 6000	1 : 25000	1 : 800	1 : 1000	1 : 1000	1 : 2000	1 : 1000	0
(VIII)	1 : 50000	1 : 50000	0	0	0	0	0	0
(IX)	1 : 200000	1 : 100000	1 : 100000	1 : 6000	1 : 6000	1 : 6000	0	0
(X)	1 : 50000	1 : 12000	1 : 6000	1 : 50000	1 : 12000	1 : 25000	1 : 3000	1 : 400
(XI)	1 : 125000	1 : 60000	1 : 30000	0	0	0	0	0
(XIV)	1 : 4000000	1 : 1000000	1 : 500000	1 : 16000	1 : 16000	1 : 30000	1 : 30000	1 : 1000
(XV)	1 : 6000	1 : 1600	1 : 1600	1 : 1600	1 : 800	1 : 800	1 : 800	1 : 400
(XVI)	1 : 2000	0	0	0	0	0	1 : 1000	1 : 1000

* As in the Russian. It may refer to the staining properties of the organism.

1,3-Cyclohexanedione (60 g) and then the above bromo compound were added to a solution of sodium methoxide prepared from 12.5 g of sodium and 30 ml of methanol. The solution was boiled for two hours and then evaporated to dryness in a vacuum. The residue was treated with 3% sodium hydroxide solution and extracted with ether. When cool, the alkaline layer was acidified with dilute hydrochloric acid, and the precipitate formed was recrystallized from 80% methanol. We obtained 23.4 g of 2-(3-methyl-2-dodecenyl)--1,3-cyclohexanedione (V), m.p. 95-96°. Found: C 77.90; 78.20; H 10.90; 11.10%. $C_{19}H_{32}O_2$. Calculated: C 78.03; H 11.03%.

When boiled with acetic anhydride, as described previously [1], 2-(3-methyl-2-dodecenyl)-1,3-cyclohexanedione gave the enol acetate (IX); b.p. 162-164° (0.05 mm); n_D^{20} 1.4860; yield 93%. Found: C 75.37; 75.40; H 10.11; 10.10%. $C_{21}H_{31}O_3$. Calculated: C 75.40; H 10.25%.

The 2,4-dinitrophenylhydrazone had m.p. 108-109° (from a mixture of methanol and dioxane). Found: N 11.37; 11.33%. $C_{27}H_{38}N_4O_6$. Calculated: N 10.88%.

3-Undecanoyloxy-2-cyclohexen-1-one (X). 1) A mixture of the potassium derivative of 1,3-cyclohexanedione, prepared from 6 g of 1,3-cyclohexanedione, and 10 g of undecanoyl chloride in 50 ml of benzene was boiled for two hours. After removal of solvent the residue was treated with sodium carbonate solution and extracted with ether. Two vacuum distillations gave 3 g of 3-undecanoyloxy-2-cyclohexen-1-one (X), b.p. 168-172° (2 mm) and n_D^{20}1.4685. Found: C 72.80; 73.02; H 10.12; 10.23%. $C_{17}H_{28}O_3$. Calculated: C 72.82; H 10.06%.

Its 2,4-dinitrophenylhydrazone had m.p. 90-91° (from methanol). Found: N 12.53; 12.40%. $C_{23}H_{32}O_6N_4$. Calculated: N 12.17%.

2) A mixture of the silver derivative of 1,3-cyclohexanedione, prepared from 3 g of 1,3-cyclohexanedione, and 5 g of undecanoyl chloride in 30 ml of benzene was boiled for two hours. After filtration and removal of solvent, the residue was vacuum-distilled. We obtained 3.3 g of 3-undecanoyloxy-2-cyclohexen-1-one.

4-Undecanoylresorcinol. A mixture of 10 g of resorcinol, 10 g of undecanoic acid, and 10 g of anhydrous zinc chloride was heated at 150-160° for two hours. After washes with water and isooctane and crystallization of the residue from a mixture of isooctane and benzene we obtained 5 g of 4-undecanoylresorcinol, m.p. 68-70°. Found: C 73.72; 73.77; H 9.29; 9.29%. $C_{17}H_{26}O_3$. Calculated: C 73.34; H 9.41%.

4-Undecylresorcinol. A mixture of 10 g of 4-undecanoylresorcinol, 20 g of amalgamated zinc, 5 ml of acetic acid, and 100 ml of 1 : 1 hydrochloric acid was boiled until the reaction to ferric chloride was negative (3-4 hours); the reduction product was extracted with ether, and after removal of ether, the crystalline reaction product was washed with isooctane. We obtained 8 g of 4-undecylresorcinol, m.p. 74-75° (from isooctane). Found: C 77.01; 77.25; H 10.81; 10.84% $C_{17}H_{28}O_2$. Calculated: C 77.22; H 10.67%.

Dimethyl Ether of 4-Undecylresorcinol. With vigorous stirring, 40 g of dimethyl sulfate was added in portions to a mixture of 8 g of 4-undecylresorcinol and 14 g of sodium hydroxide in 50 ml of water at 65-70°. The reaction product was extracted with ether, solvent was removed, and the residue was distilled. We obtained 6.5 g of the dimethyl ether of 4-undecylresorcinol, b.p. 182-185° (2 mm) and n_D^{19} 1.4962. Found: C 77.81; 77.75; H 10.88; 10.94%. $C_{19}H_{32}O_2$. Calculated: C 78.03; H 11.03%.

4-Undecyl-1,3-cyclohexanedione (XI). 1) 4-Undecylresorcinol (5.8 g) was hydrogenated in a solution of 1.3 g of potassium hydroxide in 25 ml of water and 15 ml of alcohol over 6 g of Raney nickel. In the course of six hours about 300 ml (21°, 745 mm) of hydrogen was absorbed. The solution was filtered off, acidified with dilute hydrochloric acid, treated with excess of sodium bicarbonate, and extracted with ether. On acidification of the alkaline solution with hydrochloric acid a precipitate formed and was filtered off, washed with isooctane, and crystallized from the same solvent. We obtained 2 g of 4-undecyl-1,3-cyclohexanedione (XI), m.p. 60-61°. Found: C 76.30; 76.48; H 11.29; 11.41% $C_{17}H_{30}O_2$. Calculated: C 76.64; H 11.35%.

2) Sodium (5 g) was added in portions with simultaneous gradual addition of the calculated amount of alcohol to 5 g of the dimethyl ether of 4-undecylresorcinol in 500 ml of liquid ammonia and 100 ml of ether. After removal of solvents the residue was mixed with dilute hydrochloric acid. The mixture was kept at room temperature for 12 hours and then treated with an excess of sodium bicarbonate solution. On subsequent acidification with hydrochloric acid we succeeded in isolating only traces of 4-undecyl-1,3-cylohexanedione.

Enol Acetate of 4-Undecyl-1,3-cyclohexanedione (XII) or (XIII). A mixture of 2.8 g of 4-undecyl-1,3-cyclohexanedione (XI) and 15 ml of acetic anhydride was boiled for one hour. Vacuum fractionation gave 2.4 g of a liquid of b.p. 196-201° (3 mm), by the freezing of which we isolated 0.5 g of crystalline enol acetate, m.p. 39-41° (from isooctane). Found: C 73.64; 73.78; H 10.31; 10.31%. $C_{19}H_{32}O_3$. Calculated: C 73.98; H 10.46%.

2-Bromo-4-undecyl-1,3-cyclohexanedione (XIV). A mixture of 1 g of 4-undecyl-1,3-cyclohexanedione (XI) and 0.8 g of N-bromosuccinimide in 10 ml of carbon tetrachloride was boiled for 30 minutes, the solution was vacuum-evaporated to dryness, and the residue was treated with water and isooctane. The resulting precipitate was crystallized from isooctane. We obtained 0.8 g of 2-bromo-4-undecyl-1,3-cyclohexanedione, m.p. 87-89°. Found: Br 22.80; 22.91%. $C_{17}H_{29}O_2Br$. Calculated: Br 23.19%.

SUMMARY

1. By the alkylation of 1,3-cyclohexanedione with 1-bromo-3-methyl-2-dodecene, 2-(3-methyl-2-dodecenyl)-1,3-cylohexanedione (V) was obtained, and with acetic anhydride this gave the corresponding enol acetate (IX). In the reaction of undecanoyl chloride with a metal derivative of 1,3-cyclohexanedione, 3-undecanoyloxy-2-cyclohexen-1-one (X) was formed. Reduction of 4-undecylresorcinol gave 4-undecyl-1,3-cyclohexanedione (XI), from which, by reaction with N-bromosuccinimide, 2-bromo-4-undecyl-1,3-cyclohexanedione (XIV) was obtained.

2. The diketones (IV) and (V), and also 4-undecyl-1,3-cyclohexanedione (XI) and its 2-bromo derivative (XIV), have high bacteriostatic activity in vitro toward human and avian tubercle bacilli. The diketone (IV) and its enol acetate (VIII) have appreciable activity against coccus-type bacteria. The diketone (IV) and 2-bromo-4-undecyl-1,3-cyclohexanedione (XIV) show considerable activity toward the acid-stable saprophyte B_S.

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*Original Russian pagination. See C. B. translation.

CHEMISTRY OF ACETALS

COMMUNICATION 1. GENERAL METHOD FOR THE SYNTHESIS OF BIS [DIETHYL ACETALS] OF β-DICARBONYL COMPOUNDS*

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From 1949 onward many American [1-7], Japanese [8-13], and Canadian [14-16] patents appeared on the application of the condensation of orthoformic esters with various vinyl ethers as a method for the synthesis of the corresponding acetals of malonaldehyde. Only recently has this reaction been described in greater detail [17, 18], and the method received the most systematic and complete treatment in the paper of Protopopova and Skoldinov [18].

With the object of synthesizing bis [diethyl acetals] of various β-dicarbonyl compounds required by us for use in the lengthening of isoprenoid chains, we studied the addition of triethyl orthoformate to vinyl ethers of the following types: 1) β-substituted vinyl ethers, i.e., ethyl propenyl ether, 2-bromovinyl ethyl ether, ethyl 3-methyl-1-butenyl ether, and ethyl 2-methylpropenyl ether; 2) α-substituted vinyl ethers, i.e., ethyl isopropenyl ether and ethyl 1-methylpropenyl ether; 3) one cyclic vinyl ether, i.e., 1-ethoxycyclohexene. It was found that ethyl propenyl and 2-bromovinyl ethyl ethers react readily and smoothly with orthoformic ester in equimolecular proportions in presence of catalytic amounts of boron trifluoride etherate, zinc chloride, or other catalyst of the Friedel-Crafts type (e.g., aluminum chloride, tin tetrachloride, titanium tetrachloride) with formation of methyl-1-and bromo-malonaldehyde bis [diethyl acetals], respectively, in high yield (70-80%):

$$RCH{=}CHOC_2H_5 + CH(OC_2H_5)_3 \longrightarrow (C_2H_5O)_2CHCHRCH(OC_2H_5)_2$$
$$R = CH_3,\ Br$$

In both cases the formation occurred also of small amounts of higher-boiling products, probably secondary products of the addition of the vinyl ether to the dialdehyde bis [diethyl acetal]. The structure of the methylmalonaldehyde bis [diethyl acetal] was confirmed by its conversion by reaction with hydrazine into known 4-methylpyrazole [19], which was identified as its picrate. The structure of the bromomalonaldehyde bis[diethyl acetal] was confirmed by comparison with data in the literature for bromomalonaldehyde bis [diethyl acetal] prepared in a different way and also by acid hydrolysis into the well-known crystalline bromomalonaldehyde, identified by a mixture melting point test with a known sample [21].

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The addition of orthoformic ester to 3-methyl-1-butenyl and 2-methylpropenyl ethyl ethers occurs less vigorously and gives the corresponding isopropyl- and dimethyl-malonaldehyde bis [diethyl acetals] in yields of 20-30%. In this case the greater part of the vinyl ether is recovered unchanged from the reaction. The structures of the bis [diethyl acetals] were confirmed by acid hydrolysis to the corresponding dialdehydes, which, without being isolated, were oxidized with potassium permanganate to the known isopropyl- [22] and dimethyl- [23] malonic acids.

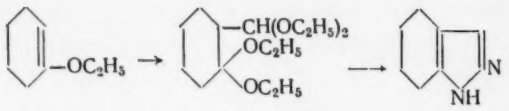
α-Substituted vinyl ethers differ appreciably from β-substituted ethers in the conditions required for reaction with orthoformic ester. It was found that in the case of α-substituted vinyl ethers only zinc chloride has a satisfactory catalytic effect. The use of boron trifluoride etherate leads to the resinification of the α-substituted vinyl ether, and titanium tetrachloride, tin tetrachloride, aluminum chloride etherate, and other catalysts bring about cleavage side reactions, which result in the formation of a complex mixture of low-boiling products, which we did not investigate more closely. Also, in reactions with α-substituted vinyl ethers it is essential to use not less than a two-fold excess of orthoformic ester. Thus, in the reaction of ethyl isopropenyl ether and of ethyl 1-methylpropenyl ether with orthoformic ester at a ratio of 1 : 2 in presence of zinc chloride at 35-45°, we obtained the bis [diethyl acetals] of acetoacetaldehyde and 2-methylacetoacetaldehyde in yields of about 45%:

$$RCH{=}C(R')OC_2H_5 + CH(OC_2H_5)_3 \longrightarrow (C_2H_5O)_2CHCHRC(OC_2H_5)_2R$$
$$R' = CH_3;\quad R = H \text{ or } CH_3$$

It must be mentioned that in both cases we obtained up to 10% of secondary reaction products, whose structures will be the subject of future communications.

The structure of the acetoacetaldehyde bis [diethyl acetal], which has been mentioned previously only in a patent [24], was confirmed by its conversion into the known 3 (or 5)-methylpyrazole [25], which was identified as its picrate and as its complex salt with silver nitrate. To confirm the structure of the 2-methylacetoacetaldehyde bis [diethyl acetal] it was converted into 4,5 (or 3)-dimethylpyrazole [26], which was identified as its picrate.

Apart from the examples examined above, we made a detailed study of the reaction between 1-ethoxycyclohexene and orthoformic ester. This reaction is again catalyzed only by zinc chloride, and to obtain the maximum yield (about 30%) of 2-oxocyclohexanecarboxaldehyde bis [diethyl acetal] it is necessary to use a considerable excess of orthoformic ester (3-4 moles per mole of 1-ethoxycyclohexene) and an equimolecular amount of zinc chloride.



In this reaction there was formed also a considerable amount of secondary condensation products, the study of which is continuing. On increase in the amount of zinc chloride to above the equimolecular amount, the yield of 2-oxocyclohexanecarboxaldehyde bis [diethyl acetal] diminishes and a considerable amount of resinous products is formed. The structure of the 2-oxocyclohexanecarboxaldehyde bis [diethyl acetal] was confirmed by its conversion into 4,5,6,7-tetrahydro-1H-indazole [27] by reaction with hydrazine in acid medium.

We showed that, apart from the catalysts mentioned in the literature, zinc chloride is a good catalyst for the reaction of ethyl vinyl ether. It is interesting that in the reaction of orthoformic ester with ethyl vinyl ether at a ratio of 1 : 1 at 40-50° in presence of titanium tetrachloride a considerable amount (up to 31%) of 1,1,3,5,5-pentaethoxypentane is formed.

We showed that orthoacetic ester is also able to react with ethyl vinyl ether. The best results were obtained by the use of a mixed catalyst (boron trifluoride etherate and zinc chloride) by heating the mixture at 50-60° for six hours. Under these conditions the above-described acetoacetaldehyde bis [diethyl acetal] was formed in 30% yield:

$$CH_2{=}CHOC_2H_5 + CH_3C(OC_2H_5)_3 \longrightarrow CH_3C(OC_2H_5)_2CH_2CH(OC_2H_5)_2$$

We also tried to bring some vinyl esters into reaction with orthoformic ester. It was found that vinyl acetate with orthoformic ester at 30-40° only in presence of a mixture of boron trifluoride etherate and yellow mercuric oxide, and as a result of double decomposition malonaldehyde bis [diethyl acetal] is formed in 25% yield; by the addition of small amounts of trichloroacetic acid to the reaction mixture the yield can be raised to 40-50%. All attempts to cause 1-cyclohexen-1-ol acetate to react were unsuccessful.

As diketene can be regarded as a peculiar internal vinyl ester, we decided to examine the action of orthoformic ester on this substance. Although diketene reacted readily with orthoformic ester in presence of boron trifluoride etherate, the reaction occurred not with addition at the double bond, but with cleavage of the ester linkage of diketene and formation of a crystalline enol ether (I). The enol ether (I) formed beautiful white crystals having a strong smell of aniseed, m.p. 29-30°; it was found to be identical with ethyl 3-ethoxycrotonate, as prepared previously by Claisen [28], and by reaction with 2,4-dinitrophenyl-hydrazine it gave the 2,4-dinitrophenylhydrazone of acetoacetic ester.

$$CH_3C{=}CH \underset{O-CO}{|\quad|} \xrightarrow{HC(OC_2H_5)_3} CH_3C{=}CHCOOC_2H_5 \quad (I)$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\quad OC_2H_5$$

As we were interested in the possibility of the addition of orthoformic ester to activated double bonds, we investigated its addition to styrene, which could lead to β-ethoxyhydrocinnamaldehyde diethyl acetal:

$$C_6H_5CH{=}CH_2 + CH(OC_2H_5)_3 \longrightarrow C_6H_5CH(OC_2H_5)CH_2CH(OC_2H_5)_2$$

It is known [29] that acetaldehyde diethyl acetal readily adds to styrene with formation of 3-ethoxy-3-phenyl-1-propanol. On the other hand a patent was taken out by Copenhaver [30] for the addition of ortho esters to butene, indene, and cyclopentadiene, and in another patent by the same author [31] it is stated that orthothioformic ester adds to styrene in presence of boron trifluoride etherate when the mixture is heated at 50° for six hours. When treated with 2,4-dinitrophenylhydrazine the product gave the 2,4-dinitrophenylhydrazone of cinnamaldehyde, but the yield is not stated. We carried out a detailed investigation of the reaction of orthoformic ester with styrene. In spite of wide variation of reaction conditions (temperature, time, relative amounts of reactants, introduction of solvents, use of various iodic and free-radical catalysts), the yield of β-ethoxyhydrocinnamaldehyde diethyl acetal did not exceed 5% on the original amount of styrene, and most of the styrene was recovered unchanged.

EXPERIMENTAL

Starting Materials. Ethyl vinyl ether: a commercial preparation was purified by treatment with and distillation over sodium; b.p. 35-36°; n_D^{20} 1.3775. 2-Bromovinyl ethyl ether was prepared by the elimination of hydrogen bromide from 1,2-dibromoethyl ethyl ether with the aid of N,N-diethylaniline [32]; b.p. 44-46° (20 mm); n_D^{20} 1.4728. The remaining vinyl ethers were prepared by the elimination of alcohol from the corresponding acetals, prepared by the reaction of aldehydes and ketones with tetraethyl orthosilicate in presence of phosphoric acid [33] and by Claisen's method [28], using p-toluenesulfonic acid instead of phosphorus pentoxide.

Ethyl Propenyl Ether. A mixture of 164 g of propionaldehyde diethyl acetal (b.p. 120-123°; $n_D^{18.5}$ 1.3900), 0.2 g of p-toluenesulfonic acid, and 8 ml of quinoline was boiled in a flask fitted with a 50-cm column; the distillate was collected in a receiver containing aqueous sodium carbonate solution. The organic layer was washed with sodium carbonate solution, dried with magnesium sulfate, treated with sodium, and after one day distilled over sodium. We obtained 68 g (66%) of ethyl propenyl ether; b.p. 69-72°; n_D^{18} 1.3990. In a similar way we prepared ethyl isopropenyl ether [from acetone diethyl acetal (b.p. 114-116°; n_D^{19} 1.3900); yield 60%; b.p. 62-64°; n_D^{24} 1.3890; ethyl 2-methylpropenyl ether [from isobutyraldehyde diethyl acetal (b.p. 134-135°; n_D^{20} 1.3940); yield 40%; b.p. 80-91°; n_D^{17} 1.4098]; ethyl 3-methyl-1-butenyl ether [from isovaleraldehyde diethyl

acetal (b.p. 64-66° at 23-25 mm); n_D^{18} 1.4020], yield 60%; b.p. 110-114°; n_D^{20} 1.4085. Found: C 74.00; 73.90; H 12.50; 12.42%. $C_7H_{14}O$. Calculated: C 73.76; H 12.36%.

Ethyl 1-Methylpropenyl Ether. This was prepared from butanone diethyl acetal (b.p. 118-122°; $n_D^{19.5}$ 1.4000); yield 70%; b.p. 89-92°; n_D^{19} 1.4060. Found: C 71.89; 71.88; H 12.21; 12.30%. $C_6H_{12}O$. Calculated: C 71.95; H 12.08%.

1-Ethoxycyclohexene. This was prepared from cyclohexanone diethyl acetal [b.p. 74-76° (14 mm); n_D^{18} 1.4320] by heating it under reduced pressure (180-190 mm) at 140-160° in presence of p-toluenesulfonic acid and quinoline; yield 77%; b.p. 57-59° (16-18 mm); $n_D^{16.5}$ 1.4592.

Catalysts. Boron trifluoride etherate was purified by distillation; b.p. 126-128°. The zinc chloride catalyst consisted of a solution of 95 g of commercial anhydrous zinc chloride in 165 g of dry ether.

Malonaldehyde Bis [Diethyl Acetal]. To a mixture of 148 g (1 mole) of orthoformic ester and 50 ml of ethereal zinc chloride we added 72 g (1 mole) of ethyl vinyl ether gradually so that the temperature did not exceed 35°. The reaction mixture was heated with stirring for two hours at 40-50°, cooled to room temperature, and washed with excess of 15-20% aqueous sodium hydroxide; the organic layer was separated, and the aqueous layer was extracted with ether. The combined organic and ether layers were dried with magnesium sulfate, and ether was distilled off. Vacuum fractionation of the residue gave 168 g (76%) of malonaldehyde bis [diethyl acetal]; b.p. 90-94° (6-7 mm); n_D^{19} 1.4070. Found: C 59.94; 59.94; H 11.00; 11.00%. $C_{11}H_{24}O_4$. Calculated: C 59.97; H 10.98.

Methylmalonaldehyde Bis [Diethyl Acetal]. A similar procedure was used. From 29.6 g (0.2 mole) of orthoformic ester and 12.9 g (0.15 mole) of ethyl propenyl ether in presence of 5 ml of ethereal zinc chloride, after the usual treatment and distillation, we obtained 25 g (70%) of methylmalonaldehyde bis [diethyl acetal]; b.p. 68-75° (1 mm); n_D^{18} 1.4152. Redistillation gave the pure bis [diethyl acetal]; b.p. 65-67° (1 mm); n_D^{18} 1.4160. Found: C 61.30; 61.20; H 11.20; 12.12%. $C_{12}H_{26}O_4$. Calculated: C 61.50; H 11.18%.

In order to prove its structure we added 23.4 g (0.1 mole) of the bis [diethyl acetal] dropwise to a mixture of 7 g (0.1 mole) of hydrazine hydrochloride, 20 ml of water, and 5 ml of 1 N HCl, and stirring was continued at 45-50° until the organic phase dissolved. When the mixture was cool, it was treated with 30% sodium hydroxide solution; the upper layer was separated, and the alkaline layer was extracted with ether. The combined upper and ether layers were dried with magnesium sulfate and, after the removal of the volatile components on a boiling water bath, the residue was vacuum-fractionated. We obtained 4 g (50%) of 4-methylpyrazole, b.p. 67-68° (2 mm) and $n_D^{16.5}$ 1.4930; the picrate prepared from this in the usual way had m.p. 147-148° (from water or benzene), which corresponds to data in the literature [19]. Found: N 22.53; 22.62%. $C_{10}H_9O_7N_5$. Calculated: N 22.51%.

Bromomalonaldehyde Bis [Diethyl Acetal]. To a mixture of 29.6 g (0.2 mole) of orthoformic ester and 2.5 ml of boron trifluoride etherate we added 30.2 g (0.2 mole) of 2-bromovinyl ethyl ether dropwise so that the temperature did not rise above 40°; the mixture was heated for one hour at 40-50°; and when it was cool 10 ml of pyridine was added. Fractionation gave 46 g (76.6%) of bromomalonaldehyde bis [diethyl acetal], b.p. 125-127° (7 mm) and 108-108.5° (3mm), n_D^{18} 1.4470, which corresponds to data in the literature [20]. Found: C 43.89; 43.96; H 7.67; 7.70%. $C_{11}H_{23}O_4Br$. Calculated: C 44.15; H 7.75%.

In order to confirm the structure, 14 g of bromomalonaldehyde bis [diethyl acetal] was stirred at 50-55° with 20 ml of 1 : 1 hydrochloric acid until it dissolved; when the mixture was cooled there was a crystalline precipitate of bromomalonaldehyde, which was filtered off, washed with ice water, and dried in a vacuum desiccator over calcium chloride. We obtained 1.8 g of bromomalonaldehyde, m.p. 136-138° (from water), undepressed by admixture of a known sample [21].

Isopropylmalonaldehyde Bis [Diethyl Acetal]. The reaction was carried out similarly with 22.2 g (0.15 mole) of orthoformic ester and 11.4 g (0.1 mole) of ethyl 3-methyl-1-butenyl ether in presence of 1.25 ml of boron trifluoride etherate. After two hours at 50-60°, 5 g of sodium carbonate was added and the mixture was stirred for 30 minutes at the same temperature and filtered. Distillation gave 5.8 g (22%) of isopropylmalonaldehyde bis [diethyl acetal]; b.p. 81-82.5° (1 mm); n_D^{18} 1.4300. Found: C 64.53; 64.50; H 11.40; 11.40%. $C_{14}H_{30}O_4$. Calculated: C 64.08; H 11.53%.

In order to confirm the structure, 7 g of the above bis [diethyl acetal] was added dropwise at not above 30° to a solution of 2.18 g of potassium permanganate in 60 ml of 1 N HCl. Manganese dioxide was filtered off, and the filtrate was acidified with concentrated hydrochloric acid and carefully extracted with ether. The ether extract was dried with magnesium sulfate and, after the removal of ether, we obtained about 1 g of isopropylmalonic acid, melting with decomposition at 87° (from benzene), which corresponds to data in the literature [22].

Dimethylmalonaldehyde Bis [Diethyl Acetal]. A mixture of 10 g (0.1 mole) of ethyl 2-methylpropenyl ether, 22.2 g (0.15 mole) of orthoformic ester, and 5 ml of ethereal zinc chloride was heated for three hours at 70° and was then left for several days at room temperature. The product was treated as in the preceding experiment. Fractionation gave 9 g (36%) of dimethylmalonaldehyde bis [diethyl acetal]; b.p. 85° (3 mm); n_D^{17} 1.4210. Found: C 62.22; 62.35; H 11.07; 11.22%. $C_{13}H_{28}O_4$. Calculated: C 62.87; H 11.37%.

The structure was confirmed as in the case of isopropylmalonaldehyde bis [diethyl acetal]. From 7 g of the dimethylmalonaldehyde bis [diethyl acetal] we obtained 1.45 g of dimethylmalonic acid, m.p. 188.5-190.5° (from benzene and petroleum ether), which corresponds to data in the literature [23]. Found: C 45.47; 45.40; H 6.00; 6.03%. $C_5H_8O_4$. Calculated: 45.45; H 6.10%.

Acetoacetaldehyde Bis [Diethyl Acetal]. a) A solution of 8.6 g (0.1 mole) of ethyl isopropenyl ether in 20 g of orthoformic ester was added dropwise at not above 45-48° to a mixture of 19.6 g (0.2 mole) of orthoformic ester and 5 ml of ethereal zinc chloride. The mixture was heated at 50-60° for three hours. After the usual treatment and fractionation we isolated 11 g (48%) of acetoacetaldehyde bis [diethyl acetal]; b.p. 73-76° (2 mm); n_D^{22} 1.4170. Found: C 61.38; 61.14; H 10.71; 10.71%. $C_{12}H_{26}O_4$. Calculated: C 61.50; H 11.18%.

b) A mixture of 16.2 g (0.1 mole) of orthoacetic ester, 1.25 ml of boron trifluoride etherate, and 10 ml of ethereal zinc chloride was stirred at 50-60° for six hours, after which the reaction product was treated with diethanolamine. Fractionation gave 7.2 g (30%) of the above-described acetoacetaldehyde bis [diethyl acetal]; b.p. 96-101° (8 mm); n_D^{20} 1.4138.

In order to confirm the structure, 18.9 g (0.08 mole) of the bis [diethyl acetal] was converted by the method described above into 4 g (60%) of 3 (or 5)-methylpyrazole; b.p. 59° (1 mm); $n_D^{16.5}$ 1.4972. The complex salt with silver nitrate prepared from this had m.p. 120°, which corresponds to data in the literature [25]. The picrate, prepared in the usual way, had m.p. 140-141° (from benzene), which corresponds to data in the literature [25]. Found: N 22.57; 22.77%. $C_{10}H_9O_7N_5$. Calculated: N 22.51%.

2-Methylacetoacetaldehyde Bis [Diethyl Acetal]. A solution of 10 g (0.15 mole) of ethyl 1-methylpropenyl ether in 10 g of orthoformic ester was added dropwise to a mixture of 22.2 g (0.15 mole) of orthoformic ester and 10 ml of ethereal zinc chloride in such a way that the temperature did not exceed 35°; the mixture was then heated at 45-50° for 90 minutes. The usual treatment and fractionation gave 11 g (44%) of 2-methylacetoacetaldehyde bis [diethyl acetal]; b.p. 100-105° (10 mm); n_D^{18} 1.4230. After redistillation the product had b.p. 103-104° (10 mm). Found: C 62.50; H 11.16%. $C_{13}H_{28}O_4$. Calculated: C 62.87; H 11.37%.

In order to confirm the structure, from 6 g (0.024 mole) of the bis [diethyl acetal] we prepared in the usual way 0.3 g of 4,5-dimethylpyrazole; b.p. 110-111° (14 mm). The picrate prepared from this had m.p. 150-152° (from a mixture of benzene and petroleum ether), which corresponds to data in the literature [26]. Found: N 21.80% $C_{11}H_{11}O_7N_5$. Calculated: N 21.54%.

2-Oxocyclohexanecarboxaldehyde Bis [Diethyl Acetal]. To a mixture of 59.2 g (0.4 mole) of orthoformic ester and a solution of 13.6 g of zinc chloride in 10 ml of dry ether we added 12.4 g (0.1 mole) of 1-ethoxycyclohexene dropwise at not above 30°; the mixture was then heated for one hour at 40°. After the usual treatment and two fractionations we isolated 8.6 g (30%) of 2-oxocyclohexanecarboxaldehyde bis [diethyl acetal]; b.p. 109-113° (7 mm); n_D^{20} 1.4527. The bis [diethyl acetal] was of low stability, so that analysis did not give satisfactory results.

In order to confirm the structure of the bis [diethyl acetal] it was condensed with hydrazine in the usual way; from 4.8 g (0.017 mole) of the bis [diethyl acetal] we obtained 0.8 g (40%) of 4,5,6,7-tetrahydro-1H-indazole, b.p. 152-153° (15 mm) and m.p. 81-82° (from petroleum ether), which corresponds to data in the literature [27]. Found: N 22.46% $C_7H_{10}N_1$. Calculated: N 22.92%.

The picrate of the tetrahydroindazole had m.p. 154.5-156° (from benzene), which corresponds to data in the literature [27]. Found: N 19.94; 19.89%. $C_{13}H_{13}O_7N_5$. Calculated: N 19.94%.

Reaction of Orthoformic Ester with Diketene. Dropwise addition was made of 50 g (0.58 mole) of diketene to a mixture of 77.8 g (0.52 mole) of orthoformic ester and 1 ml of boron trifluoride etherate at 5-7°. The mixture was left overnight at 0°, and on the next day it was heated for four hours at 40° and left at room temperature until the odor of diketene disappeared. Two fractionations gave 54 g of a product of b.p. 55-58°(3 mm), from which by strong cooling we isolated 36.8 g of crystalline ethyl 3-ethoxycrotonate, m.p. 29-30° (from petroleum ether), which corresponds to data in the literature [28]. Found: C 60.88; 60.94; H 8.98; 8.92%. $C_8H_{14}O_3$. Calculated: C 60.7; H 8.86%.

When treated with a hydrochloric acid solution of 2,4-dinitrophenylhydrazine, the crystalline product gave the 2,4-dinitrophenylhydrazone of acetoacetic ester, which showed no depression of melting point in admixture with a known sample.

SUMMARY

1. A study was made of the addition of triethyl orthoformate to some α- and β-substituted vinyl ethers and 1-ethoxycyclohexene in presence of various catalysts; this permitted the synthesis of bis [diethyl acetals] of various β-dicarbonyl compounds (substituted malonaldehyde and acetoacetaldehyde).

2. The previously undescribed bis [diethyl acetals] of methyl-, isopropyl-, and dimethyl-malonaldehydes, 2-methylacetoacetaldehyde, and 2-oxocyclohexanecarboxaldehyde were prepared and their structures were proved.

3. The condensation of orthoacetic ester with ethyl vinyl ether in presence of a mixed catalyst (boron trifluoride etherate and zinc chloride) was carried out; as a result acetoacetaldehyde bis [diethyl acetal] was obtained.

4. The reactions of orthoformic ester with diketene and with styrene were studied.

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CATALYTIC ALKYLATION OF TETRALIN

COMMUNICATION 2. ALKYLATION OF TETRALIN WITH 1-HEPTENE

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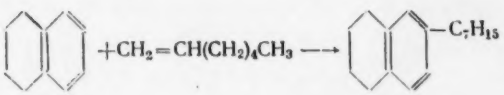
From the literature survey on the synthesis of alkyltetralins, given in our preceding communication [1], it will be seen that no investigation has yet been devoted to the preparation of heptyltetralins. As would be expected, therefore, the physical and chemical properties of these hydrocarbons are not to be found in the literature. We carried out the alkylation of tetralin with 1-heptene in a flow system in contact with a catalyst prepared by the impregnation of alumina with a solution of hydrofluoric acid; these experiments were carried out at ordinary and elevated pressures. We used also a commercial aluminum silicate catalyst that we have used previously [1] as Catalyst 5 in the catalytic synthesis of amyltetralin.



In the experiments we found the conditions under which the yield of heptyltetralin was 48.7% on the amount of 1-heptene taken. Such a yield in one passage was obtained in experiments at 200° with a space velocity for the passage of the tetralin-heptene mixture of 0.25 hr^{-1}.

EXPERIMENTAL

The original 1-heptene was prepared by the Grignard-Wurtz synthesis from butyl bromide and allyl chloride by the method described by Kazanskii, Tarasova, and Sterligov [2]. The 1-heptene had b.p. 93-94° (756 mm), n_D^{20} 1.4000, d_4^{20} 0.6981, and iodine value 357. For 1-heptene the literature gives: b.p. 93.64° (760 mm); n_D^{20} 1.3998; d_4^{20} 0.6970 [3]. The tetralin had: b.p. 205-206.5°; n_D^{20} 1.5425; d_4^{20} 0.9712 [4].

Alkylation of Tetralin in Presence of Alumina Treated with HF. The alkylation of tetralin in presence of catalysts prepared by the impregnation of alumina with hydrofluoric acid (10% and 20% HF) was carried out at atmospheric and elevated pressures. In each experiment we took 35 g (1/4 mole) of tetralin and 8.2 g (1/12 mole) of 1-heptene.

By experiments carried out in presence of this catalyst it was shown that at atmospheric pressure and 300-350° there occurs the dehydrogenation of tetralin to naphthalene and the alkylation of the latter. The yield of alkylation product of b.p. above 220° did not exceed 5%. From the combined alkylation products we isolated a fraction of b.p. 290-310° and n_D^{20} 1.5665. This fraction appeared to consist of a mixture of heptyltet-

ralin and heptylnaphthalene. At 40 atm the dehydrogenation of tetralin in presence of this catalyst was observed only at 350°. At 300° the yield of the heptyltetralin fraction [b.p. 175-180° (6 mm); n_D^{20} 1.5200; d_4^0 0.9235] was 9.1% on the tetralin and 30.5% on the 1-heptene.

Alkylation of Tetralin in Presence of an Aluminum Silicate Catalyst. In the investigation of the alkylation of tetralin with 1-heptene over an aluminum silicate catalyst we studied the effects of temperature, pressure, and molar proportions of the components on the yield of alkylation product (Tables 1-3). In each experiment we took 66 g (0.5 mole) of tetralin; 1-heptene was taken in the various amounts indicated in the tables. The catalyzates were distilled through a column of 15-plate efficiency. The fractions coming over below 100° were distilled off at atmospheric pressure, and the further distillation was carried out at 6 mm. First unchanged tetralin was distilled off; then we collected an intermediate fraction having b.p. 90-170°, a fraction of b.p. 170-190° and n_D^{20} 1.5190-1.5200, and a fraction of b.p. 190-210°. The residues, b.p. above 210°, were combined and later subjected to further fractionation.

TABLE 1. Effect of Temperature on Yield of Alkylation Product. (Pressure 40 atm; space velocity 0.25 hr^{-1}; molar ratio of tetralin to 1-heptene 3 : 1).

Expt.	Temp. (°C)	Yield of fraction (g)		
		b.p. 170-190° (6 mm)	b.p. 190-210° (6 mm)	b.p. above 210° (6 mm)
1	150	7.0	—	2.0
2	180	12.5	—	3.5
3	200	14.0	5.2	1.5
4	300	12.0	2.1	0.5
5	300	13.1	3.2	3.7

As will be seen from Tables 1-3, the optimum conditions for the alkylation of tetralin with 1-heptene in presence of an aluminum silicate catalyst with a space velocity of 0.25 hr^{-1} are: 200°; 10 atm; molar ratio of tetralin to 1-heptene 2 : 1. Under these conditions the yield of heptyltetralin fraction of b.p. 170-190° (6 mm) was 24.3% on the tetralin taken and 48.7% on the 1-heptene (Table 3, Expt. 10). The tetralin that did not react remained, in the main, unchanged; its dehydrogenation occurred only to a very small extent. From the fractions coming over up to 100°, by refractionation we obtained the following narrow fractions: Fraction I, b.p. 90-95° and n_D^{20} 1.4000; fraction II, b.p. 95-99° and n_D^{20} 1.4030. The Raman spectra of these fractions showed that Fraction I contained 40% of unchanged 1-heptene and 60% of trans-2-heptene and that Fraction II contained 30% of 1-heptene and 70% of 2-heptene, mainly the trans isomer.

On redistillation of 140 g of combined fractions of b.p. 170-190° (6 mm) and n_D^{20} 1.5190-1.5200 through a column of 40-plate efficiency at a residual pressure of 2 mm we isolated 125 g of a fraction of b.p. 134-139° n_D^{20} 1.5185 and d_4^{20} 0.9210. On distillation of this hydrocarbon at ordinary pressure it came over in the narrow range 303-304° (746 mm); found MR 75.71. $C_{17}H_{26}F_3$. Calculated MR 74.91. Found: C 88.78; H 11.26%. $C_{17}H_{26}$. Calculated: C 88.64; H 11.36%.

The position of the side chain in the monoalkyltetralins was proved by methods of infrared spectroscopy. It is known [5] that substantial differences exist between the spectra of different alkyltetralin isomers, and these permit their identification. These differences are particularly clearly marked in the region of the frequencies of deformational nonplanar CH vibrations at 10-12 μ and of their first overtones at 5-6 μ. The use of 5-6 μ region is found to be most convenient as in this region the spectra of alkyltetralins and of the corresponding (as regards substitution) benzenes are very similar.

Comparison of the infrared spectrum of the heptyltetralin that we had synthesized with those of the four isomers of ethyltetralin [5] and with those of alkylbenzenes [6] in the region of 5-6 μ showed that the side group occupied the β-position in the tetralin molecule; hence, in the hydrocarbon that we obtained the heptyl group occupied the β-position:

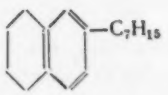
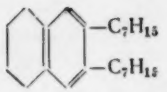


TABLE 2. Effect of Pressure on the Yield of Alkylation Product. (Temperature 200°; space velocity 0.25 hr^{-1}; molar ratio of tetralin to 1-heptene 3 : 1).

Expt.	Pressure (atm)	Yield of fraction (g)		
		b.p. 170-190° (6 mm)	b.p. 190-210° (6 mm)	b.p. above 210° (6 mm)
6	2	14.0	2.0	1.5
7	10	18.2	3.0	3.0
8	10	18.2	3.5	1.5
3	40	14.0	5.2	1.5
9	40	15.0	2.5	2.0

The combined fractions (20 g) of b.p. 190-210° (6 mm) and the residues boiling above 210° (30.5 g) were distilled at 3 mm through a column of 15-plate efficiency. We then obtained the following fractions: a) 12 g, b.p. 185-196°, n_D^{20} 1.5490, and d_4^{20} 0.9832; b) 15.2 g, b.p. 205-215°, n_D^{20} 1.5180, and d_4^{20} 0.9892. The infrared spectrum of the first fraction gave us reason to suppose that it contained an alkylnaphthalene. The spectrum picture in the region of the overtones of the deformational nonplanar CH vibrations at 5-6 μ was similar to that of 1,2,4,5-tetraethylbenzene. On the basis of this it may be supposed that this fraction consisted mainly of a β,β'-diheptyltetralin:



Analysis gave: C 88.00; 87.95; H 11.76; 11.74%. $C_{24}H_{40}$. Calculated: C 87.8; H 12.2%. The yield of this fraction, calculated on the amount of tetralin taken, was about 3%.

TABLE 3. Effect of the Molar Ratio of Tetralin to 1-Heptene on the Yield of Alkylation Product. (Temperature 200°; pressure 10 atm; space velocity 0.25 hr^{-1}).

Expt.	Amt. of heptene (g) taken for 66 g of tetralin	Molar ratio of tetralin to heptene	Yield of fraction of b.p. 170-190° (6 mm)		
			in g	in %	
				on tetralin	on 1-heptene
8	16.3	3 : 1	18.2	15.8	47.4
10	24.5	2 : 1	28.2	24.3	48.7
11	32.7	3 : 2	28.5	24.9	37.2

SUMMARY

The conditions were found for the catalytic alkylation of tetralin with 1-heptene with formation of a mixture of β-heptyltetralin and β,β'-diheptyltetralin. The yield of β-heptyltetralin was 48.7% in one passage (calculated on the amount of 1-heptene taken); this corresponds to 24.3% on the amount of tetralin taken.

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DEHYDROGENATION OF GASOLINES AND THEIR NARROW FRACTIONS IN PRESENCE OF NICKEL ON VARIOUS CARRIERS

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In our preceding communication [1] we reported the results of an investigation of the peculiar features of nickel-alumina catalysts under the conditions for the dehydrogenation of cyclohexane, individual samples of the heptane-methylcyclohexane fraction of Maikop gasoline, and unfractionated Surakhan straight-run gasoline; it was there shown that a nickel-alumina catalyst containing 30% of nickel and prepared by a procedure, improved by us, of coprecipitating nickelous and aluminum hydroxides from a solution of the nitrates with sodium hydroxide solution has high dehydrogenating activity and is very stable; this catalyst effected the aromatization of unfractionated Surakhan gasoline over a period of 249 hours without regeneration. In view of this, it was of interest to study the dehydrogenating activity and stability of nickel catalysts deposited in various ways on other carriers.

In the present paper we give the results of an investigation of the properties of a series of nickel catalysts on various carriers. As carriers we used pumice, activated charcoal, asbestos, ferric oxide, chromium oxide, zinc oxide, and silica gel, both in the pure state and in admixture with alumina. The experiments showed that on the application of nickel by the coprecipitation method on the mixed carriers $Al_2O_3 + SiO_2$ and $Al_2O_3 + Fe_2O_3$ we again obtain active dehydrogenating catalysts (see Catalyst 16, Table 3, and Catalyst 17, Table 4). However, for the dehydrogenation of cyclohexanes they are less stable than a nickel-alumina catalyst. Thus, Catalyst 16 (30% Ni + 30% SiO_2 + 40% Al_2O_3) was found to be capable of effecting the aromatization of unfractionated Tuimazin gasoline for 110 hours with eight regenerations. Catalyst 17 (50% Ni + 25% Al_2O_3 + 25% Fe_2O_3) carried out this reaction for 200 hours with seven regenerations.

EXPERIMENTAL

To determine the effect of the chemical nature of the carrier and of the conditions of deposition on the activity and stability of nickel catalysts we prepared 21 samples of nickel catalyst on various carriers. Catalysts 1-9 consisted of nickel on alumina; they differed in nickel content, in the composition of the salts used, in the precipitation conditions, and in the washing; of these, Catalysts 1,2, and 3 were precipitated from a mixture of molar solutions of nickel and aluminum nitrates with sodium carbonate solution at 60°. All of them showed feeble activity for the dehydrogenation both of cyclohexane and of narrow gasoline fractions. Catalysts 4-8 were prepared by the coprecipitation of nickelous and aluminum hydroxides from molar solutions of nickel and aluminum nitrates with 30% sodium hydroxide solution at room temperature. For the preparation of Catalyst 9 by an analogous method, as starting salts we used nickel and aluminum sulfates. Catalysts 4 and 5 were prepared by Zelinskii and Komarevskii's method [2] and Catalysts 6-9 were prepared by a method developed by us [1]. Catalysts 10 (Ni-Cr_2O_3), 12 (Ni-ZnO), 13 (Ni-Fe_2O_3), 14 (50% Ni + 25% Al_2O_3 + 25% Cr_2O_3) and 17 (50% Ni + 25% Al_2O_3 + 25% Fe_2O_3) were prepared by the coprecipitation of the corresponding nitrates with 30% sodium hydroxide under the conditions used for Catalysts 6-9.

TABLE 1. Properties of Gasoline Fractions and Unfractionated Straight-Run Gasolines

Boiling range of fraction or unfractionated gasoline	n_D^{20}	d_4^{20}	Toluene content (% by vol.)
98-103° fraction of Surakhan gasoline	1.4152	0.7530	3.0
97-103° fraction of Maikop gasoline	1.4170	0.7480	12.0
94-109° fraction of the "toluene gasoline" of No. 4 Maikop petroleum	1.4165	0.7455	7.0
98-102° fraction of "Tovarnaya Kalosha" gasoline	1.4150	0.7475	~ 1.0
40-200° unfractionated Tuimazin gasoline after treatment with $AlCl_3$ [4]	1.4128	0.7332	8.5
42-196° B-59 Groznyi gasoline	1.4050	0.7175	4.0

Catalysts 15 (50% Ni + 25% Al_2O_3 + 25% SiO_2), 16 (30% Ni + 40% Al_2O_3 + 30% SiO_2) and 11 (Ni-SiO_2) were prepared by the following method: a molar solution of sodium silicate was treated warm with molar sodium bicarbonate and carbon dioxide. The resulting gel was carefully washed with water and then impregnated with nickel nitrate solution (Catalyst 11) or a solution containing nickel and aluminum nitrates. The nitrates were then precipitated with 30% sodium hydroxide solution at room temperature with careful stirring. Catalysts 18 (50% Ni + 50% charcoal), 19 (50% Ni + 50% pumice), and 20 (50% Ni + 50% asbestos) were prepared by impregnating the carrier with concentrated nickel nitrate solution, drying at 125°, and roasting at 450° until the oxides of nitrogen were removed. After reduction with hydrogen (see below) they were all found to be of low activity. Catalyst 21 (nickel on alumina promoted with a little copper) was prepared by the precipitation of a molar solution containing nickel, copper, and aluminum nitrates with 30% sodium hydroxide solution. All the catalysts were reduced with electrolytic hydrogen with gradual rise of temperature up to 360° [3]. Reduction at 350-360° continued for 16-20 hours.

The separation of the heptane-methylcyclohexane fractions from the unfractionated gasolines was carried out through a column of 19-plate efficiency. The 98-102° fraction of "Tovarnaya Kalosha" gasoline and the "toluene gasoline" No. 4 were obtained from the Krasnodar petroleum refinery. The characteristics of the fractions isolated and of the unfractionated gasolines are given in Table 1.

The activity of each catalyst was defined by the extent of the dehydrogenation of 5-ml portions of cyclohexane [5]. The "lives" of the most active catalysts were determined by the dehydrogenation of narrow fractions of Surakhan or Maikop straight-run gasoline at 300 ± 5° at a space velocity of 0.4 hr^{-1} at atmospheric pressure. In the dehydrogenation experiments the outgoing gas consisted of pure hydrogen.

The dehydrogenation experiments were carried out in a glass tube with an internal diameter of 24 mm placed in an electric tube furnace fitted with an automatic regulator. The tube was filled with catalyst (length of layer 60 cm). The volume of reduced catalyst was usually 150 ml. In prolonged experiments the activity of the catalyst was checked periodically by the passage of cyclohexane before and after the experiments with gasoline fractions after careful displacement of the gasoline from the catalyst surface. The aromatic contents of the gasoline catalyzates were determined by the sulfuric acid method. Results of the determination of the activities of the catalysts investigated, with respect to cyclohexane and in the dehydrogenation of narrow fractions and unfractionated straight-run gasoline, are given in Table 2.

From the data presented in Table 2 it will be seen that the most active dehydrogenating catalysts are prepared by the deposition of nickel (Catalysts 5-8) or of nickel and copper (Catalyst 22) on alumina. Catalysts on mixed carriers have lower initial activities (Catalysts 14-17) than the nickel-alumina catalysts (5-8). Catalysts 10 (Ni-Cr_2O_3) and 12 (Ni-ZnO) were also less active in the dehydrogenation of cyclohexane and the heptane-methylcyclohexane fraction of Maikop gasoline. Experiment showed that an active dehydrogenating catalyst could not be obtained when the original salts used were nickel and aluminum sulfates (Catalyst 9). Catalysts prepared by the deposition of nickel on activated charcoal, pumice, and asbestos by impregnation of the carrier with nickel nitrate solution were all of low activity (Catalysts 18-20).

TABLE 2. Activities of Nickel Catalysts on Various Carriers in the Dehydrogenation of Cyclohexane and Gasoline Fractions. (Temperature 300°, space velocity 0.4 hr^{-1})

Catalyst No.	Catalyst	Extent of dehydrogenation of cyclohexane		Gasoline fraction investigated	Properties of catalyzate of gasoline fraction	
		n_D^{20} of catalyzate	benzene content of catalyzate		n_D^{20}	toluene content (% by vol.)*
1	40% Ni + 60 Al_2O_3	1,4561	49,5	98—103° fraction of Surakhan gasoline	1,4198	12,0
2	the same	1,4454	33,8	the same	1,4168	4,5
3	50% Ni + 50% Al_2O_3	1,4504	41,5	» »	1,4200	12,0
4	Ni — Al_2O_3 (Zelinskii and Komarevskii's method)	1,4554	48,2	» »	1,4317	25,0
5	the same	1,4907	90,0	» »	1,4450	43,5
6	50% Ni + 50% Al_2O_3	1,4939	93,4	98—102° fraction of "Tovarnaya Kalosha" gas.	1,4560	61,0
7	the same	1,4972	97,0	98—103° fraction of Surakhan gasoline	1,4452	44,0
8	30% Ni + 70% Al_2O_3	1,4934	92,8	the same	1,4450	44,0
9	50% Ni + 50% Al_2O_3	1,4300	7,0	» »	—	—
10	50% Ni + 50% Cr_2O_3	1,4816	79,8	94—109° fraction of "toluene gasoline" No. 4	1,4370	38,5
11	50% Ni + 50% SiO_2	1,4547	47,4	the same	1,4198	15,0
12	50% Ni + 50% ZnO	1,4743	72,4	» »	1,4268	24,0
13	50% Ni + 50% Fe_2O_3	1,4380	21,8	» »	—	—
14	50% Ni + 25% Al_2O_3 + 25% Cr_2O_3	1,4702	67,1	94—109° fraction of "toluene gasoline" No. 4	1,4312	37,0
15	50% Ni + 25% Al_2O_3 + 25% SiO_2	1,4708	68,3	the same	1,4270	25,0
16	30% Ni + 40% Al_2O_3 + 30% SiO_2	1,4906	90,0	Unfractionated Tuimazin gasoline	1,4198	25,0
17	50% Ni + 25% Al_2O_3 + 25% Fe_2O_3	1,4865	85,7	94—109° fraction of "toluene gasoline" No. 4	1,4491	50,0
18	50% Ni + 50% active charcoal	1,4390	23,4	—	—	—
19	50% Ni + 50% pumice	1,4354	17,2	98—103° fraction of Surakhan gasoline	1,4167	12,0
20	50% Ni + 50% asbestos	1,4354	17,2	the same	1,4165	12,0
21	67,5% Ni + 2,5% Cu + 30% Al_2O_3	1,4980	97,6	Unfractionated Tuimazin gasoline	1,4198	25,0

*Including natural aromatics, see Table 1.

TABLE 3. Stability of Catalyst 16 (30% Ni + 30% SiO_2 + 40% Al_2O_3) in the Aromatization of Unfractionated Tuimazin Gasoline

Stage of work	Amt. of aromatized gasoline (ml)	Extent of dehydrogenation of cyclohexane	
		n_D^{20} of catalyzate of initial expt.	conversion of cyclohexane into benzene (%)
Before regeneration	760	1.4906	90.0
After first regeneration	835	1.4995	99.4
After second regeneration	735	1.4989	98.6
After third "	760	1.4985	98.2
After fourth "	760	1.4875	86.5
After fifth "	735	1.4890	88.2
After sixth "	610	1.4876	86.6
After seventh "	685	1.4824	81.4
After eighth "	685	1.4726	70.2
	6565		

TABLE 4. Stability of Catalyst 17 (50% Ni + 25% Al_2O_3 + 25% Fe_2O_3) in the Aromatization of Groznyi Gasoline and Fractions of Maikop Gasoline

Stage of work	Gasoline investigated	Amt. of aromatized gasoline (ml)	Toluene content of combined catalyzate	Extent of dehydrogenation of cyclohexane	
				n_D^{20} of catalyzate of initial expt.	conversion of cyclohexane into benzene (%)
Before first regeneration	Unfractionated Groznyi B-59	1200	29 – 22	1.4865	86.0
After first "	94-109° fraction of Maikop "toluene gasoline" No. 4	675	50 – 29	1.4992	98.2
After second "	Ditto	1425	50 – 24.5	1.4950	94.4
After third "	97-103° fraction of Maikop gasoline	675	50 – 36	1.4897	89.1
After fourth "	Ditto	900	50 – 34	1.4769	75.0
After fifth "	"	1650	43.5 – 34	1.4694	66.6
After sixth "	"	4500	35 – 25	1.4729	70.7
After seventh "	"	975	39 – 25	1.4781	76.6
		12,000			

Data on the activity and stability of Catalysts 16 and 17 are given in Tables 3 and 4. The results of experiments with Catalysts 10, 14, and 15 are shown in Fig. 1. The characteristics of the work of Catalysts 5, 6, 8, and 22 are given in our previous papers [1, 6]. The data in Table 3 show that a 30% nickel catalyst on a mixed carrier (SiO_2 + Al_2O_3) (Catalyst 16) was able to carry out the aromatization of unfractionated Tuimazin gasoline for a period of 110 hours. In this time 6.56 liters of Tuimazin gasoline was aromatized with eight regenerations. The combined catalyzate boiled over the range 48-200° and had n_D^{20} 1.4270 and d_4^{20} 0.7579; it contained 28% of aromatic hydrocarbons, and with 1.5 ml of tetraethyllead it had an octane rating of 67.0, instead of 64 before aromatization.

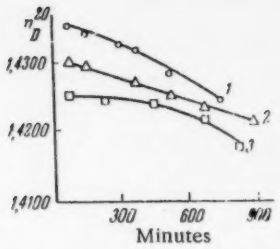

Fig. 1. Change in activity of Catalyst 10 (Curve 1), Catalyst 14 (Curve 2), and Catalyst 15 (Curve 3) in the aromatization of narrow fractions of Maikop gasoline.

The results given in Table 4 show that Catalyst 17 was extremely active and stable in the aromatization of Groznyi gasoline and the 94-109° and 97-103° fractions of Maikop gasoline; it carried out the reaction for 200 hours with seven regenerations. As a result of the aromatization of the fractions investigated catalyzates were obtained with a toluene content of 25-50% by volume.

SUMMARY

1. An investigation was made of the effect of the chemical nature of the carrier on the activities and stabilities of nickel catalysts for the dehydrogenation of cyclohexanes contained in gasolines. The chemical nature of the carrier has a substantial effect on the catalytic properties of a nickel catalyst.

2. The most active and stable catalysts are obtained by the deposition of nickel on alumina. Even when mixed catalysts having alumina as a component were used ($Al_2O_3 + SiO_2$ and $Al_2O_3 + Fe_2O_3$), relatively active and stable dehydrogenating catalysts were obtained (Catalysts 16 and 17, Table 2).

3. As a result of the aromatization of gasoline fractions of Maikop petroleum in presence of a nickel catalyst on a mixed carrier (Catalyst 17), catalyzates with a toluene content of 25-50% by volume were obtained.

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*Original Russian pagination. See C. B. translation.

POISONING OF A PLATINUM CATALYST BY THIOPHENE UNDER REFORMING CONDITIONS

COMMUNICATION 3. EFFECT OF TEMPERATURE AND PRESSURE OF HYDROGEN

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July, 1960
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In our previous communications [1, 2] we gave the results obtained in the investigation of the poisoning of 1% and 5% platinum-alumina catalysts as a function of the concentration of thiophene in the original cyclohexane. All these experiments were carried out in a flow system under a hydrogen pressure of 20 atm and at a temperature of 450°. It was shown [2] that the general laws governing the poisoning were similar for the 1% and the 5% platinum catalyst. The use of thiophene containing radioactive sulfur and the application of radiochemical analysis enabled us to make a precise determination for the first time of the amount of sulfur deposited on the catalyst in the poisoning process and to establish that the relation between the increase of the sulfur content of the catalyst and the reduction in catalyst activity is a linear one. It was shown also that the regeneration of deactivated catalysts is accompanied by the removal of sulfur from their surfaces, but complete restoration of activity is already attained with the removal of 60% of the sulfur deposited on the catalyst during its poisoning. In the present paper we describe an investigation of the poisoning of a 1% $Pt - Al_2O_3$ catalyst at various temperatures and hydrogen pressures.

EXPERIMENTAL

The catalyst used in this work contained 1% of platinum deposited on alumina. The preparations of the original alumina and of the catalysts are described in [1]. It must be stated that the portion of catalyst prepared for the present work was somewhat less active and more sensitive to the action of thiophene than that previously prepared [1]

Three series of experiments on the dehydrogenation of cyclohexane containing 2.65% of thiophene were carried out in a flow-type apparatus. The first series was carried out at a constant hydrogen pressure (20 atm) and at temperatures of 425°, 450°, 475°, and 500°. The other two series were carried out at 450° and 475° at hydrogen pressures of 10, 20, 30, and 40 atm. In all experiments the space velocity was $2\ hr^{-1}$ and the hydrogen: hydrocarbon ratio was 5. Any change in the benzene content of the catalyzates in the course of the experiments was checked refractometrically [3]. The gases leaving the apparatus were purified from hydrogen sulfide as described previously [1] and were analyzed in a VTI apparatus. To remove dissolved hydrogen sulfide from the catalyzate, the latter was shaken with zinc sulfate solution. The amounts of hydrogen sulfide isolated from the gas and removed from the catalyzate (in the form of zinc sulfide)were determined iodometrically. The sulfur content of the catalyzate after purification from hydrogen sulfide was determined by the lamp method [4]. The deactivated catalysts were heated for one hour in a vacuum at 100-120°, and their specific surfaces were determined by the dynamic method [5].

All the experimental results are given in Tables 1 and 2 and Figures 1 and 2. It will be seen from Table 1 that at all temperatures investigated the dehydrogenating activity of 1% Pt – Al_2O_3 falls sharply during the first 1-2 hours to a definite value and becomes stabilized at this value. Hence, these data fully confirm the results of our previous investigations [1, 2]. The relation of the yield of benzene from cyclohexane containing 2.65% of thiophene to temperature is presented in Fig. 1 [Curve (a)]. Fig. 1 also gives results on the conversion of pure cyclohexane into benzene at various temperatures [Curve (b)]. From Table 1 and Fig. 1 it follows that the extent of the dehydrogenation of cyclohexane over a catalyst of stabilized activity increases from 5.5% at 425° to 37.6% at 500°. In Table 2 we give the results obtained in a study of the deactivation of the same 1% Pt – Al_2O_3 catalyst as a function of pressure at two temperatures, 450° and 475°. It will be seen that in Experiments 22 and 26 the dehydrogenating power of the catalyst does not remain constant in the usual way, but gradually diminishes throughout the whole experiment. This great deactivation of the catalyst is probably due to the relatively low hydrogen pressure (10 atm). Change in pressure from 10 to 20 atm leads to an increase in the yields of benzene from 3.9% to 13.9% at 450° and from 11.6% to 20.2% at 475°, and in the last case the catalyst activity remained constant throughout each experiment.

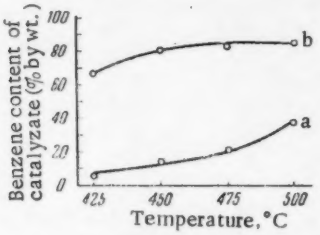

Fig. 1. Relation of extent of dehydrogenation of cyclohexane to temperature: a) cyclohexane containing 2.65% of thiophene; b) pure cyclohexane.

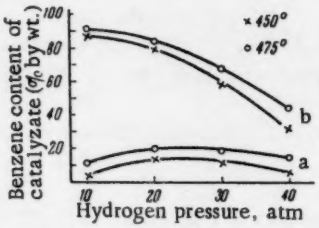

Fig. 2. Relation of extent of dehydrogenation of cyclohexane to hydrogen pressure in system: a) cyclohexane containing 2.65% of thiophene; b) pure cyclohexane.

It is known from thermodynamics that with increase in pressure the conversion of cyclohexane diminishes. On the other hand, as Meerboot and co-workers showed [6], the toxicity of sulfur compounds for reforming catalysts falls with increase in hydrogen pressure. Fig. 2 shows the relation of benzene yield, both from pure cyclohexane and from cyclohexane containing 2.65% of thiophene, to pressure [Curves (a) and (b) respectively] for 450° and 475°. It will be seen that in the case of pure cyclohexane with increase in pressure from 10 to 40 atm the original dehydrogenating power of the catalyst changes from 86.6% to 32.9% at 450° and from 91.4% to 44.8% at 475°. On the other hand, on dehydrogenation of cyclohexane containing 2.65% of thiophene it was found that, both at 450° and at 475°, with increase in pressure the benzene content of the catalyzate [Curve (a)] rises at first and then, in the range 20-40 atm, falls somewhat.

As stated above, in almost all of the experiments we made a quantitative determination of the sulfur leaving the apparatus with the gases in the form of hydrogen sulfide and of the sulfur remaining in the catalyzate. These results are presented in Tables 1 and 2. It should be pointed out that in the present work we succeeded in detecting traces of undecomposed thiophene only in Experiment 21 at 425° with a hydrogen pressure of 20 atm. Table 1 shows that with rise in temperature the amount of hydrogen sulfide isolated from the gas increases and the amount of hydrogen sulfide simultaneously present in the catalyzate diminishes. Hence, rise in temperature leads to more complete decomposition of the thiophene added to the original hydrocarbon. Increase in pressure leads to an analogous result (Table 2).

Measurement of the specific surfaces of the deactivated catalysts by the dynamic method [5] showed that with change in the temperature in the experiments from 425° to 600° there is a change in surface from 205 to 145 sq.m/g. This is possibly associated with increase in the cracking power of the catalyst and therefore with the deposition of increased amounts of coke on the catalyst surface resulting from the rise in temperature. As Table 2 shows, increase in pressure at a given temperature has scarcely any effect on the specific surfaces of the spent catalysts.

TABLE 1. Deactivation of a 1% Pt – Al_2O_3 Catalyst in the Dehydrogenation of Cyclohexane in Presence of Thiophene at Various Temperatures (hydrogen pressure = 20 atm; v = 2 hr^{-1}; hydrogen : hydrocarbon = 5; thiophene content of cyclohexane = 2.65%)

Expt. No.	Temperature expt. in °C	Extent of dehydrogenation of cyclohexane into benzene (% by wt.)								Extent of dehydrogenation of cyclohexane after 20 hr (% on original value)	Amount of sulfur separated (% on amount introduced in catalyst) from:		Specific surface of catalyst in m^2/g
		originally	after								gas	catalyzate	
			10 min	30 min	1 hr	5 hr	10 hr	15 hr	20 hr				
21	425	66,5	36,0	14,2	5,5	5,5	5,5	5,5	5,5	8,3	90,5	2,7	205
18	450	80,1	55,1	33,0	21,1	13,6	14,2	13,4	13,9	17,4	91,9	2,4	180
19	475	82,8	46,4	28,1	20,8	20,0	20,2	20,2	20,2	24,3	92,4	2,0	170
20	500	85,0	78,4	62,0	39,0	37,4	36,9	37,6	37,6	44,2	93,3	1,2	145

TABLE 2. Deactivation of a 1% Pt – Al_2O_3 Catalyst in the Dehydrogenation of Cyclohexane in Presence of Thiophene at Various Hydrogen Pressures and at 450° and 457°. (v = 2 hr^{-1}; hydrogen : hydrocarbon = 5; thiophene content of cyclohexane = 2.65%)

Expt. No.	Temperature expt. in °C	Hydrogen pressure in atm	Extent of dehydrogenation of cyclohexane into benzene (% by wt.)								Extent of dehydrogenation of cyclohexane after 20 hr (% on original value)	Amount of sulfur separated (% on amount introduced in catalyst) from:		Specific surface of catalyst in m^2/g
			originally	after								gas	catalyzate	
				10 min	30 min	1 hr	5 hr	10 hr	15 hr	20 hr				
22	450	10	86,6	43,4	23,7	22,8	18,9	11,0	6,0	3,9	8,3	—	—	182
18	450	20	80,1	55,1	33,0	21,1	13,6	14,2	13,4	13,9	17,4	91,9	2,4	180
23	450	30	59,0	46,2	21,4	12,0	11,5	11,5	11,5	11,5	21,3	—	—	186
24	450	40	32,9	21,1	9,9	8,9	7,2	8,2	7,2	7,2	21,9	—	—	189
26	475	10	91,4	61,0	44,1	31,3	20,3	14,4	12,4	11,6	12,7	92,2	2,6	176
19	475	20	82,8	46,4	28,1	20,8	20,9	20,2	20,2	20,2	24,3	92,4	2,0	170
27	475	30	68,1	52,0	36,5	20,3	19,4	18,4	18,5	18,5	29,8	93,5	1,3	172
28	475	40	44,8	41,9	19,4	15,4	15,4	15,4	15,7	15,4	34,3	93,9	1,2	173

SUMMARY

1. An investigation was made of the deactivation of 1% Pt – Al_2O_3 as a function of temperature (425-500°) at a constant hydrogen pressure of 20 atm and as a function of pressure (10-40 atm) at 450° and 475° in the course of the dehydrogenation of cyclohexane containing 2.65% of thiophene.

2. The extent of the dehydrogenation of cyclohexane at pressures of 20, 30, and 40 atm and at various temperatures (425°, 450°, 475°, and 500°) becomes stabilized after 1-2 hours. However, at a pressure of 10 atm at 450° and 475° no stabilization of the extent of dehydrogenation is observed and the activity of the catalyst gradually falls over a period of 20 hours.

3. The stabilized extent of dehydrogenation of cyclohexane increases with rise in temperature (from 425° to 500°) and diminishes with increase in pressure (from 20 to 40 atm).

4. The specific surfaces of deactivated catalysts fall with rise in temperature, but are scarcely changed by change in pressure.

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POLYENES

COMMUNICATION 11*. UNSYMMETRICAL 1, 6-DIARYL 1, 3, 5-HEXATRIENES

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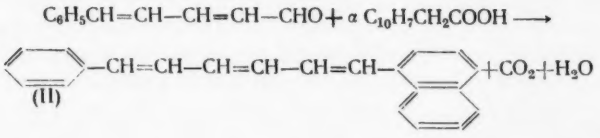
The simple method which we have described for the preparation of 5-phenyl-2,4-pentadienal [1] from cinnamaldehyde diethyl acetal and ethyl vinyl ether has made wide application of this aldehyde, which was previously not readily accessible, in the synthesis of various compounds. In particular, from this compound one may prepare various unsymmetrical 1, 6-disubstituted 1, 3, 5-hexatrienes, which have as yet received little study and are of interest for the study of the relation between the structure and the fluorescence properties of these compounds.

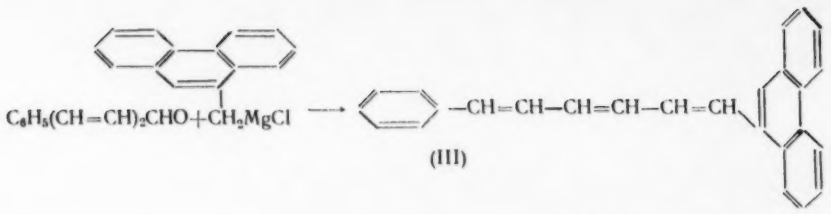
In the present paper we give the synthesis of the following compounds: 1,6-diphenyl-, 1-(1-naphthyl)-6-phenyl-, 1-(9-phenanthryl)-6-phenyl-, 1-(4-biphenylyl)-6-phenyl-, 1-phenyl-6-(2-pyridyl)-, and 1-phenyl-6-(2-quinolyl)-1,3,5-hexatrienes. These hexatrienes were prepared by the action on 5-phenyl-2,4-pentadienal of either organometallic compounds or the corresponding arylacetic acids by Kuhn's method [2]. Thus, the important 1,6-diphenyl-1,3,5-hexatriene (I) may be prepared by the action on 5-phenyl-2,4-pentadienal of benzylmagnesium chloride, benzylsodium, or phenylacetic acid. The most convenient preparative method for this hydrocarbon is reaction between the aldehyde and phenylacetic acid.

In the same way, from 5-phenyl-2,4-pentadienal and 1-naphthalene-acetic acid we obtained 1-(1-naphthyl)-6-phenyl-1,3,5-hexatriene (II), which showed bright fluorescence, both in solutions and in the crystalline state, and thus differs from 1,6-diphenyl-1,3,5-hexatriene, which does not fluoresce in the crystalline state:



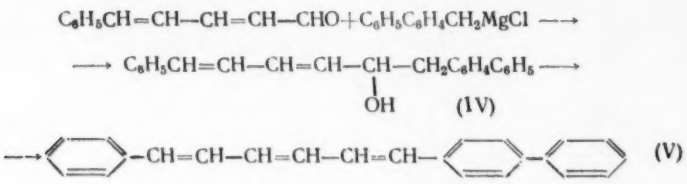
By the action of 5-phenyl-2,4-pentadienal on (9-phenanthryl)methyl-magnesium chloride we synthesized 1-(9-phenanthryl)-6-phenyl-1,3,5-hexatriene (III) in the form of strongly fluorescent colorless crystals:

*For Communication 10 see Izvest. Akad. Nauk SSSR, Otel. Khim. Nauk 372 (1960). [C. B. translation].



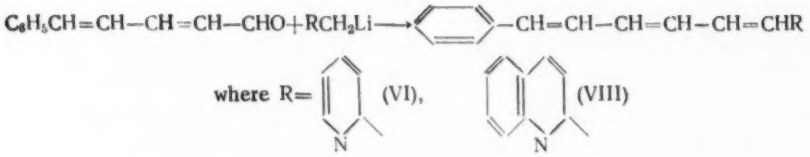
(III)

As shown previously [3], the quantum yield of the fluorescence of 1-phenyl-6-p-tolyl-1,3,5-hexatriene in benzene and heptane is higher than for the corresponding solutions of 1,6-diphenyl-1,3,5-hexatriene. It was of interest to determine the effect produced on the brightness of the fluorescence of the introduction of phenyl, instead of methyl, into the p-position of one of the phenyls of 1,6-diphenyl-1,3,5-hexatriene. With this object we synthesized 1-(4-biphenylyl)-6-phenyl-1,3,5-hexatriene. On reaction between 5-phenyl-2,4-pentadienal and p-phenylbenzylmagnesium chloride we obtained 1-(4-biphenylyl)-6-phenyl-3,5-hexadien-2-ol (IV), which on boiling with glacial acetic acid was converted into 1-(4-biphenylyl)-6-phenyl-1,3,5-hexatriene (V), which was strongly fluorescent in benzene solution:



(V)

To determine the effect of the presence of nitrogen-containing heterocycles on the fluorescence of hexatrienes we synthesized hexatrienes containing heterocyclic substituents. Thus, by the action of (2-pyridyl)-methyllithium on 5-phenyl-2,4-pentadienal we obtained 1-phenyl-6-(2-pyridyl)-1,3,5-hexatriene (VI), and by the reaction of the same aldehyde with (2-quinolyl)methyllithium we succeeded in isolating 6-phenyl-1-(2-quinolyl)-3,5-hexadien-2-ol (VII), which when boiled with a mixture of acetic acid and hydrochloric acids was converted into 1-phenyl-6-(2-quinolyl)-1,3,5-hexatriene (VIII):



The fluorescence of (VI) and (VIII) was weaker than that of the aryl derivatives of 1,3,5-hexatriene.

The results of the investigation of the optical properties of the products will be reported later.

EXPERIMENTAL

1,6-Diphenyl-1,3,5-hexatriene (I). 1. A solution of 13 g (0.082 mole) of 5-phenyl-2,4-pentadienal [1] in 60 ml of dry ether was added over a period of one hour to a solution of a Grignard reagent prepared from 13.9 g (0.11 mole) of benzyl chloride, 2.88 g (0.12 g-atom) of magnesium, and 100 ml of dry ether. A precipitate formed during the addition of the aldehyde, but in the subsequent two hours at room temperature this went completely into solution. The reaction mixture was decomposed with 25% ammonium chloride solution, and the ether layer was washed with water and dried. After removal of ether we obtained an orange-red viscous oil, which was heated for 90 minutes with 400 ml of ethanol and 38 ml of 40% hydrobromic acid. From the cooled solution we filtered 12.1 g of 1,6-diphenyl-1,3,5-hexatriene, m.p. 153-176°. After chromatography on alumina, 1,6-diphenyl-1,3,5-hexatriene formed pale-yellow crystals, m.p. 199-201° (yield 5 g, i.e., 26.5%). The literature [2] gives m.p. 200°.

2. A solution of 11.53 g (0.073 mole) of 5-phenyl-2,4-hexadienal in 25 ml of toluene was added over a period of 25 minutes to a solution of benzylsodium prepared from 11.2 g (0.1 mole) of chlorobenzene, 4.6 g (0.2 g-atom) of sodium, and 35 ml of toluene. After the usual treatment and distillation of toluene we obtained 17.3 g of a viscous oil, which was heated with alcohol and HBr as described for the preceding experiment. After chromatography on alumina we isolated 5.35 g (31.5%) of 1,6-diphenyl-1,3,5-hexatriene, m.p. 199-200.5°.

3. A mixture of 4.74 g (0.03 mole) of 5-phenyl-2,4-pentadienal, 4.08 g (0.03 mole) of phenylacetic acid, 3.5 g litharge, and 4 ml of acetic anhydride was boiled in a stream of nitrogen for 4.5 hours. When cooled to room temperature, the reaction mixture crystallized, and the precipitate was filtered off and washed, twice with alcohol and once with a mixture of equal parts of ethanol and acetone. We obtained 2.1 g of 1,6-diphenyl-1,3,5-hexatriene, m.p. 198-200°. We isolated a further 0.3 g of the hydrocarbon from the mother liquor. Yield 2.4 g (34.5%). On dilution of the mother liquor with water, lead phenylacetate separated, and this, after several crystallizations from acetone and then from dioxane, was a crystalline substance, m.p. 198-199°. Found: C 40.50; 40.32; H 3.00; 3.08; ash 46.54; 46.31%. $C_{16}H_{14}O_4Pb$. Calculated: C 40.25; H 2.96; ash 46.75%.

1-(1-Naphthyl)-6-phenyl-1,3,5-hexatriene (II). A mixture of 4.1 g (0.026 mole) of 5-phenyl-2,4-pentadienal, 4.9 g (0.026 mole) of 1-naphthaleneacetic acid, 3 g of litharge, and 4 ml of acetic anhydride was refluxed for five hours. When cool, the mixture crystallized to form a thick slurry, which was diluted with 5 ml of ethanol. The precipitate was filtered off and washed with a mixture of equal amounts of benzene and ethanol. We obtained 1.5 g (20.4%) of 1-(1-naphthyl)-6-phenyl-1,3,5-hexatriene, m.p. 150-154°. After chromatography on alumina the hydrocarbon was obtained in the form of bright-yellow crystals, m.p. 159-160°. Found: C 93.40; 93.36; H 6.58; 6.51%. $C_{22}H_{18}$. Calculated: C 93.57; H 6.43.

1-(9-Phenanthryl)-6-phenyl-1,3,5-hexatriene (III). A solution of 2.28 g (0.01 mole) of 9-(chloromethyl)-phenanthrene in 40 ml of a mixture of equal amounts of dry ether and benzene together with a few drops of ethyl bromide was added to 0.3 g of magnesium, and the whole was boiled for one hour in a water bath. A solution of 1.58 g (0.01 mole) of 5-phenyl-2,4-pentadienal in 10 ml of dry ether was added to the cooled Grignard reagent. The mixture was boiled for 30 minutes, kept at room temperature for two hours, and decomposed with ammonium chloride solution. The undissolved precipitate of di-9-phenanthryl-ethane was filtered off, washed with alcohol, and dried; m.p. 249-251°; yield 1.1 g (57.5%). The literature [4] gives m.p. 251-253°.

The benzene-ether solution was washed with water and dried over potassium carbonate. After removal of solvent we obtained 1.74 g of pale-yellow oil, which was boiled with 50 ml of ethanol and 0.5 ml of HBr for 3.5 hours. From the cooled solution we filtered 0.29 g of 1-(9-phenanthryl)-6-phenyl-1,3,5-hexatriene, m.p. 239-245°, and on evaporation of the mother liquor we obtained a further 0.35 g of the hydrocarbon, which melted at 240-246° after crystallization from toluene. Yield 0.56 g (39.5%). After chromatography on alumina and recrystallization from toluene, 1-(9-phenanthryl)-6-phenyl-1,3,5-hexatriene formed colorless crystals having a blue fluorescence, m.p. 253-253.5°. Found: C 94.12; 93.77; H 5.96; 6.00%. $C_{26}H_{20}$. Calculated: C 93.94; H 6.06%.

1-(4-Biphenylyl)-6-phenyl-3,5-hexadien-2-ol (IV). A solution of 2 g (0.0126 mole) of 5-phenyl-2,4-pentadienal in 10 ml of dry ether was added over a period of 20 minutes to a Grignard reagent prepared from 2.6 g (0.0128 mole) of p-phenylbenzyl chloride, 0.4 g of magnesium, and 10 ml of dry ether. The mixture was kept at room temperature for 30 minutes and then decomposed with ammonium chloride. The ether was distilled off, and the oily residue crystallized out. We obtained 1.9 g (46.5%) of 1-(4-biphenylyl)-6-phenyl-3,5-hexadien-2-ol, m.p. 125-145°, which, after two crystallizations from ethanol and then from ethyl acetate, had m.p. 133-136°. Found: C 88.67; 88.51; H 6.51; 6.56%. $C_{24}H_{22}O$. Calculated: C 88.30; H 6.80%.

1-(4-Biphenylyl)-6-phenyl-1,3,5-hexatriene (V). A solution of 0.5 g of 1-(4-biphenylyl)-6-phenyl-3,5-hexadien-2-ol in 10 ml of glacial acetic acid was boiled for 15 minutes. When the solution was cool we filtered off 0.46 g (almost quantitative yield) of a yellow precipitate of 1-(4-biphenylyl)-6-phenyl-1,3,5-hexatriene, which melted at 228-229° after crystallization from xylene. Found: C 93.10; 93.10; H 6.60; 6.73%. $C_{24}H_{20}$. Calculated: C 93.46; H 6.54%.

1-Phenyl-6-(2-pyridyl)-1,3,5-hexatriene (VI). A solution of 6.8 g (0.072 mole) of 2-picoline in 15 ml of dry ether was added to a solution of phenyllithium prepared from 11 g (0.07 mole) of bromobenzene, 1.1 g of lithium, and 70 ml of dry ether. After one hour a solution of 9.48 g (0.06 mole) of 5-phenyl-2,4-pentadienal in 15 ml of ether was added over a period of 45 minutes to the cooled solution of (2-pyridyl)methyllithium, and

the mixture was then stirred further for two hours. The precipitate formed was filtered off (20.2 g) and was gradually added with stirring to 200 ml of 4% hydrochloric acid. The acid solution was neutralized with sodium carbonate, and the oil that separated was boiled for one hour with a mixture of 60 ml of acetic and 10 ml of hydrochloric acids. After being cooled, the solution was poured into water and neutralized with ammonia. The precipitate was filtered off and washed with a mixture of equal amounts of ethanol and acetone. We obtained 4.5 g of 1-phenyl-6-(2-pyridyl)-1,3,5-hexatriene, m.p. 140-156°, which, after several crystallizations from alcohol, melted at 175-180°; yield 2.13 g (15.2%). After chromatography on alumina 1-phenyl-6-(2-pyridyl)-1,3,5-hexatriene formed slightly yellowish crystals, m.p. 178.5-180°. Found: C 87.56; 87.66; H 6.51; 6.60; N 6.29; 6.00%. $C_{17}H_{15}N$. Calculated: C 87.51; H 6.48; N 6.01%.

6-Phenyl-1-(2-quinolyl)-3,5-hexadien-2-ol(VII). A solution of 4.74 g (0.03 mole) of 5-phenyl-2,4-pentadienal in 15 ml of ether was added over a period of 45 minutes to an ethereal solution of (2-quinolyl)-methyllithium prepared from 4.29 g (0.03 mole) of quinaldine and an equimolecular amount of phenyllithium. The mixture was stirred at room temperature for one hour and decomposed with water. We filtered off 1.9 g (20%) of the precipitated 6-phenyl-1-(2-quinolyl)-3,5-hexadien-2-ol; after several crystallizations from ethanol this formed yellow crystals, m.p. 145-146°. Found: C 83.66; 83.50; H 6.55; 6.24; N 5.06; 5.13%. $C_{21}H_{19}NO$. Calculated: C 83.69; H 6.36; N 4.65%.

1-Phenyl-6-(2-quinolyl)-1,3,5-hexatriene (VIII). A solution of 0.6 g of 6-phenyl-1-(2-quinolyl)-3,5-hexadien-2-ol in 3 ml of glacial acetic acid and 0.5 ml of concentrated hydrochloric acid was boiled for one hour, after which it was poured into cold water and neutralized. We obtained 0.48 g (almost quantitative yield) of 1-phenyl-6-(2-quinolyl)-1,3,5-hexatriene, m.p. 148-157°. After chromatography on alumina and crystallization from benzene, 1-phenyl-6-(2-quinolyl)-1,3,5-hexatriene formed bright-yellow needles, m.p. 161-162°, which fluoresced in ultraviolet radiation. Found: C 88.72; 88.88; H 6.07; 6.08; N 5.14; 5.13%. $C_{21}H_{17}N$. Calculated: C 89.01; H 6.05; N 4.94%.

SUMMARY

1. Some new unsymmetrical 1,6-disubstituted 1,3,5-hexatrienes containing aromatic and heterocyclic substituents were synthesized.

2. Convenient methods were found for the preparation of 1,6-diphenyl-1,3,5-hexatriene from 5-phenyl-2,4-hexadienal.

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SYNTHESIS OF PYRIDINE BASES FROM 1-BUTEN-3-YNE

COMMUNICATION 2. PREPARATION OF COLLIDINES*

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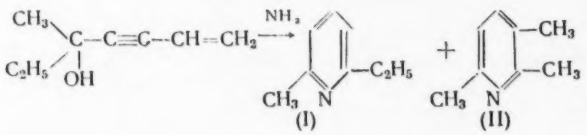
In the preceding communication [1] we reported the preparation of pyridine bases by the catalytic condensation of 2-methyl-5-hexene-3-yn-2-ol with ammonia. We then obtained 2,4- and 2,6-lutidines and s-collidine. In continuation of this work we investigated the condensation of 3-methyl-6-heptene-4-yn-3-ol with ammonia over a $CdO-Al_2O_3$ (30 : 70) catalyst. It was found that in this case the course of the reaction was more complex than in the condensation of 2-methyl-5-hexen-3-yn-2-ol with ammonia, and from the reaction products we isolated 6-ethyl-2-picoline (I) and 2,3,6-trimethylpyridine (II):



Thus, under optimum conditions with passage over this catalyst of a mixture of 3-methyl-6-hepten-4-yn-3-ol and ammonia in the molar ratio 1 : 3 at 400° at a space velocity of 1.4 (with respect to the alcohol) we obtained bases in 32.2% yield (on the alcohol), which contained 27.7% of 6-ethyl-2-picoline (I) and 42.5% of 2,3,6-trimethylpyridine (II). In this reaction the yields of bases were low because of the simultaneous dehydration and isomerization of the alcohol.

The literature [2] shows that, on being heated strongly, 4-penten-2-ynyl alcohols may split up into the original 1-buten-3-yne and carbonyl compound. This was confirmed in our experiments on the condensation of 5-hexen-3-yn-2-ol and 6-hepten-4-yn-3-ol with ammonia, in which there were considerable amounts of acetonitrile and propionitrile among the reaction products (this will be described in detail in a future communication).

On the assumption that the formation of pyridine bases can proceed by condensation with the butanone and 1-buten-3-yne formed by the decomposition of 3-methyl-6-hepten-4-yn-3-ol, we carried out the condensation of ammonia with 1-buten-3-yne and butanone. Pyridine bases were in fact obtained, and the yield was considerably higher than in the case of 3-methyl-6-hepten-4-yn-3-ol. Thus the passage of a mixture of 1-buten-3-yne, butanone, and ammonia in the molar proportions 1 : 3 : 7.5 over $CdO-Al_2O_3$ (30 : 70) or

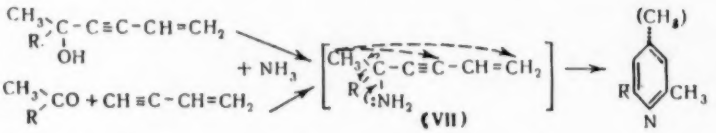
*The communication [1] is to be regarded as Communication 1 of this series.

$Cd_3(PO_4)_2$-Al_2O_3 (20 : 80) at the optimum temperature of 400° at a space velocity of 0.33 (with respect to 1-buten-3-yne) leads to the formation of pyridine bases in 79.6% yield (on the 1-buten-3-yne), containing 10.4% of 6-ethyl-2-picoline (I), 57.5% of 2,3,6-trimethylpyridine (II), and 29.5% of 2,3,5,6-tetramethylpyridine (III). The formation of the tetramethylpyridine (III) is probably to be attributed to the condensation of excess of butanone with ammonia, and this was shown to be so by special experiments in which on passage of ammonia with butanone in absence of 1-buten-3-yne over a $Cd_3(PO_4)_2$-Al_2O_3 (20 : 80) catalyst at 400° we obtained the pyridine (III) and traces of the pyridine (II). Oparina [3] has stated that the pyridine (III) is formed in the condensation of butanone with formaldehyde and ammonia; the yields obtained by her differ little from those obtained by us.

The high yield of pyridine bases obtained by the condensation of butanone with 1-buten-3-yne and ammonia prompted us to carry out a series of similar experiments based on acetone. It was found that acetone and 1-buten-3-yne readily react with ammonia over CdO-Al_2O_3 (30 : 70) and $Cd_3(PO_4)_2$-Al_2O_3 (20 : 80) at 350-450° with formation of three pyridine bases, namely 2,6-lutidine (IV), 2,4-lutidine (V), and s-collidine (VI). Under optimum conditions over CdO-Al_2O_3 at 400° with proportions of 1-buten-3-yne, acetone, and ammonia of 1 : 3 : 6.7 and at a space velocity of 0.21 (with respect to 1-buten-3-yne) we obtained a mixture of bases in 65% yield, and this contained 75% of the pyridine (IV), 16.5% of the pyridine (V), and 7% of the pyridine (VI). Hence, the yield of the pyridines (IV), (V), and (VI) was in this case 2-2.5 times as great as that which we obtained by the condensation of 2-methyl-5-hexen-3-yn-2-ol with ammonia [1].

It is interesting that the proportions of the pyridines (IV), (V), and (VI) obtained by the condensation of 1-buten-3-yne, acetone, and ammonia coincided exactly with the proportions of the same pyridines obtained from 2-methyl-5-hexen-3-yn-2-ol and ammonia. This probably indicates a common mechanism for the two reactions. An attempt to obtain pyridine bases by the condensation of ammonia separately with acetone or 1-buten-3-yne under our conditions was not successful.

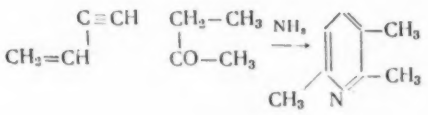
The formation of 6-ethyl-2-picoline (I), and also of (IV) and (V), probably proceeds via the intermediate formation of the 4-penten-2-ynylamine (VII), which may be obtained both from 2-methyl-5-hexen-3-yn-2-ol and 3-methyl-6-hepten-4-yn-3-ol, on the one hand, and from ketones, ammonia, and 1-buten-3-yne by a reaction analogous to that of Mannich with subsequent ring closure to the pyridine, on the other:



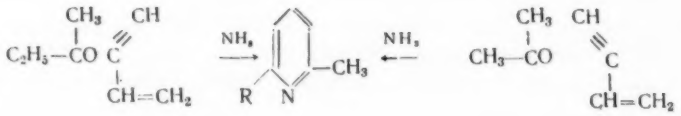
(VII)

where R = CH_3 or C_2H_5

The formation of 2,3,6-trimethylpyridine from 1-buten-3-yne, ammonia, and butanone can easily be represented as follows:



The formation of the pyridines (I) and (IV) may be explained by an analogous scheme:



Dehydration products from 4-penten-2-ynyl alcohols cannot be regarded as intermediaries in this reaction, since it was shown that the condensation of 2-methyl-1,5-hexadien-3-yne (dehydration product of 2-methyl-5-hexen-3-yn-2-ol) with ammonia did not give pyridine bases.

EXPERIMENTAL

The syntheses of pyridine bases were carried out in a quartz tube filled with 40 ml of catalyst and placed in a tube furnace. The temperature of the process was measured with a thermocouple in the middle of the catalyst layer. The organic reactants were passed in from an electrolytic dosimeter, and ammonia was fed from a cylinder. The reaction products were trapped in traps cooled with ice water. The catalyzate was treated with hydrochloric acid (1 : 1), and the neutral products were separated. The acid solution was washed with ether, and the bases were liberated with sodium hydroxide; the bases were extracted with ether, dried with fused potassium hydroxide, and distilled from a Favorskii flask.

The $Cd_3(PO_4)_2$-Al_2O_3 (20 : 80) catalyst was prepared by the impregnation of granulated (2 × 2 × 2) commercial alumina with cadmium acetate, drying, and conversion of cadmium acetate into the phosphate with a solution of trisodium phosphate. The catalyst granules were washed free from sodium ions (flame test), the catalyst was dried at 100-110°, and it was then roasted in a stream of air at 500°. The $CdHPO_4$-$CaHPO_4$ (20 : 80) catalyst was prepared by adding the calculated amount of ammonia to a solution of calcium acetate, cadmium nitrate, and phosphoric acid taken in the proportions required to give a catalyst of the composition indicated; the product was washed, dried, and roasted at 500°. The method of preparing the cadmium oxide catalyst was given in the preceding communication.

After each experiment the catalyst was regenerated by passage of air for 2-3 hours at 500°. 3-Methyl-6-hepten-4-yn-3-ol [b.p. 64-65° (10 mm) and n_D^{20} 1.4805] was synthesized from butanone and 1-buten-3-yne [4] by Iotsich's method.

Catalytic Treatment of 3-Methyl-6-hepten-4-yn-3-ol with Ammonia. This was carried out over the CdO-Al_2O_3 catalyst. The effect of temperature and space velocity of the feed of the alcohol on the yield of catalyzate and pyridine bases is shown in Table 1. The effect of the molar ratio of alcohol and ammonia was studied for the case of 2-methyl-5-hexen-3-yn-2-ol, and it was shown that an optimum yield is obtained at a molar ratio of ammonia to alcohol of 3 : 1; further increase of this ratio does not affect the yield of bases. In view of this, in the case of 3-methyl-6-hepten-4-yn-3-ol a threefold excess of ammonia was again used. For identification purposes, 34 g of the mixture of bases obtained at 400° at a space velocity of 1.4 hr^{-1} and a molar ratio of alcohol to ammonia of 1 : 3 was fractionated through a column of 25-plate efficiency. We then obtained Fraction I, b.p. 158-161°, 27.7%; Fraction II, b.p. 168-170°, 42.5%; and also the first runnings and the residue.

Fraction I, b.p. 158-161° (730 mm), n_D^{20} 1.4944 (picrate m.p. 126-127°, picrolonate, m.p. 164-166°), consisted of 6-ethyl-2-picoline (I).

The literature gives: b.p. 160° and n_D^{25} 1.4921 [5]; picrate, m.p. 126-127°, [6]; picrolonate, m.p. 165-166° [7].

Fraction II, b.p. 168-170° (730 mm) and n_D^{20} 1.5030 (picrate, m.p. 177°), consisted of 2,3,6-trimethylpyridine (II).

Picrate: Found: N 16.11%; $C_{14}H_{14}N_4O_7$; calculated: N 15.99%. The literature [7] gives: b.p. 173° (743 mm); picrate, m.p. 177-178°.

Catalytic Treatment of a Mixture of 1-Buten-3-yne, Butanone, and Ammonia. This was carried out over the $Cd_3(PO_4)_2$-Al_2O_3 (20 : 80) catalyst. 1-Buten-3-yne was prepared by heating 2-methyl-5-hexen-3-yn-2-ol with 2% of potassium hydroxide powder in a boiling water bath; it was washed free from acetone with water, dried with calcium chloride, and condensed in traps at -20°; yield 74%. The boiling point of the 1-buten-3-yne obtained was 5°.

A mixture of the organic reactants was prepared by dissolving the calculated amount of 1-buten-3-yne in butanone, and it was passed into the catalysis tube from the dosimeter, which was cooled with ice water. The relation of the yield of pyridine bases to the reaction temperature and to the space velocity of feed of the reaction mixture is shown in Table 2.

TABLE 1

Effect of Experimental Conditions on the Yield of Pyridine Bases from 3-Methyl-6-hepten-4-yn-3-ol and Ammonia over $CdO-Al_2O_3$. (Molar ratio of alcohol to NH_3 = 1 : 3)

Expt.	Reaction temp. (°C)	Space velocity of feed of alcohol (hr^{-1})	Yield of catalyzate (%)	Yield of bases (% on alcohol)
Effect of temperature				
1	300	1.4	71.0	25.6
2	360	1.4	77.3	32.0
3	400	1.4	75.0	32.2
4	450	1.4	68.3	22.3
5	480	1.4	56.0	23.4
Effect of rate of feed of reaction mixture				
6	360	0.94	75.1	24.7
7	360	1.4	77.3	32.0
8	360	1.65	73.0	30.2
9	360	1.9	76.4	21.3

By fractionation through a column, 105.5 g of pyridine bases obtained by the passage of a mixture of 1-buten-3-yne, butanone, and ammonia in the molar proportions 1 : 3 : 7.5 over $Cd_3(PO_4)_2-Al_2O_3$ (20 : 80) at 400° and at a space velocity of 0.33 hr^{-1} (with respect to 1-buten-3-yne) gave the fractions: Fraction I, b.p. 158-161°, 10.4%; Fraction II, b.p. 168-172°, 57.7%; Fraction III, b.p. 195-203°; 29.5%.

Fraction I, b.p. 158-161° (730 mm) and n_D^{20} 1.4940 (picrate, m.p. 126-127°; picrolonate, m.p. 164.5-166°), consisted of 6-ethyl-2-picoline (I). A mixture test of the picrate with the sample prepared from 3-methyl-6-hepten-4-yn-3-ol showed no depression of melting point.

Fraction II, b.p. 168-172° (730 mm) and n_D^{20} 1.5030 (picrate, m.p. 177°) consisted of 2,3,6-trimethylpyridine (II). A mixture test of the picrate with the sample prepared from 3-methyl-6-hepten-4-yn-3-ol showed no depression of melting point.

Fraction III, b.p. 195-203° (730 mm) and m.p. 78-80° (picrate, m.p. 173-174°) consisted of 2,3,5,6-tetramethylpyridine (III).

Picrate: Found: N 15.52%; $C_{15}H_{16}N_4O_7$; Calculated: N 15.37%. The literature [7] gives: b.p. 197-198° and m.p. 81°; picrate, m.p. 173.5°.

The catalyst $Cd_3(PO_4)_2-Al_2O_3$ works without loss in activity for two hours, and it fully recovers its activity in a two-hour regeneration at 500° in a stream of air. In the catalytic treatment of 1-buten-3-yne, and also of a benzene solution of 1-buten-3-yne, with ammonia over a $Cd_3(PO_4)_2-Al_2O_3$ catalyst under optimum conditions, no pyridine bases were obtained.

Condensation of 1-Buten-3-yne with Ammonia over $Cd_3(PO_4)_2-Al_2O_3$. This was carried out at 400-410° at a rate of feed of ammonia of 30 liters/min and a space velocity of 1.32 hr^{-1} (with respect to butanone). From 210 g of butanone we obtained 34 g of bases, from which by fractionation through a column we isolated 12.4% of Fraction I, b.p. 168-176° (735 mm), and 34% of Fraction II, b.p. 190-200° (735 mm). Fraction I was obtained in 1.6% yield (on the ketone); after six recrystallizations from alcohol, its picrate had m.p. 176-177°, undepressed by admixture of the picrate of 2,3,6-trimethylpyridine. Fraction II (yield 3% on the ketone) was a crystalline substance, m.p. 80° after two sublimations. In admixture with 2,3,5,6-tetramethylpyridine there was no depression of melting point.

Catalytic Treatment of 1-Buten-3-yne and Acetone with Ammonia. This was carried out over the following catalysts: $Cd_3(PO_4)_2-Al_2O_3$ (20 : 80), $CdO-Al_2O_3$ (30 : 70), $CdHPO_4-CaHPO_4$ (20 : 80), and commercial alumina. As the experiments showed (Table 3), the highest yields of pyridine bases were obtained over $Cd_3(PO_4)_2-Al_2O_3$ and $CdO-Al_2O_3$.

The optimum conditions for the reaction were determined over $CdO-Al_2O_3$, and the data are presented in Table 4. Fractionation through a column of 25-plate efficiency of 59 g of pyridine bases obtained by passage of a solution of 1-buten-3-yne in acetone together with ammonia in the molar proportions of 1 : 3 : 6.7 over $CdO-Al_2O_3$ at 380° at a space velocity of 0.21 hr^{-1} (with respect to 1-buten-3-yne)gave the following fractions: Fraction I, b.p. 141-142° (743 mm), 74.5%, Fraction II, b.p. 150-153° (743 mm), 16.5%; Fraction III, b.p. 168-175° (743 mm), 7.1%.

Fraction I, b.p. 141-142° (743 mm) and n_D^{20} 1.4968 (picrate, m.p. 162-162.5°), consisted of 2,6-lutidine. The melting point of a mixture with an authentic sample was not depressed. Fraction II, b.p. 150-153° (743 mm), n_D^{20} 1.5030 (picrate, m.p. 181°), consisted of 2,4-lutidine. A mixture with authentic picrate had m.p. 181°. Fraction III, b.p. 168-175° (743 mm) and n_D^{20} 1.4983 (picrate, alone and in admixture with authentic sample, m.p. 154-155°), consisted of s-collidine.

TABLE 2

Effect of Experimental Conditions on the Yield of Pyridine Bases from 1-Buten-3-yne, Butanone, and Ammonia. (Rate of feed of ammonia 30 liter/hr)

Expt. No.	Molar ratio of 1-buten-3-yne: ketone	Reaction temperature, °C	Space velocity of feed of reaction mixture in hr^{-1}	Yield of catalyzate (% on reaction mixture passed)	Yield of bases (% on 1-buten-3-yne)
			Effect of temperature		
1	1 : 4	300	1,3	91,2	25,3
2	1 : 4	350	1,3	95,7	41,9
3	1 : 4	400	1,3	97,8	79,6
4	1 : 4	450	1,3	84,5	68,3
5	1 : 4	475	1,3	77,0	65,9
6	1 : 4	530	1,3	56,5	43,5
			Effect of rate of feed of reaction mixture		
7	1 : 4	400	0,5	91,7	66,3
8	1 : 4	400	1,0	95,3	73,8
9	1 : 4	400	1,3	97,8	79,6
10	1 : 4	400	1,6	96,8	69,9
			Effect of molar ratio of reactants		
11	1 : 1	400	1,3	88,7	50,2*
12	1 : 2	400	1,3	90,0	56,0
13	1 : 3	400	1,3	94,0	69,2**
14	1 : 4	400	1,3	97,8	79,6
15	1 : 6	400	1,3	86,1	61,2

*Yield on ketone 67.1%.

**Yield on ketone 40.5%.

TABLE 3

Relation of the Yield of Pyridine Bases to the Composition of the Catalyst under Optimum Conditions. (Rate of feed of ammonia 30 liters/min) (r.m. = reaction mixture)

Catalyst	Molar ratio 1-buten-3-yne : ketone	Reaction temperature in °C	Space velocity of feed of r. m.	Yield of catalyzate (% on r.m.)	Yield of bases (% on 1-buten-3-yne)
$Cd_3(PO_4)_2/Al_2O_3$	1 : 3	380	1,4	77,4	62,6
CdO/Al_2O_3	1 : 3	400	1,4	73,1	64,7
$CdHPO_4/CaHPO_4$	1 : 3	400	1,4	61,5	34,1
Al_2O_3	1 : 3	400	1,4	68,1	12,6

TABLE 4

Effect of Conditions on Yield of Bases in the Condensation of Acetone and 1-Buten-3-yne with Ammonia.

Expt. No.	Molar ratio 1-buten-3-yne: ketone	Reaction temperature in °C	Space velocity of feed of reaction mixture in hr^{-1}	Yield of catalyzate in %	Yield of bases (% on 1-buten-3-yne)
		Effect of temperature			
1	1:3	300	1,4	85,6	58,8
2	1:3	350	1,4	78,8	60,3
3	1:3	380	1,4	73,1	64,7
4	1:3	400	1,4	74,5	62,3
5	1:3	450	1,4	68,0	47,1
		Effect of molar ratio of reactants			
6	1:1	380	1,4	68,2	23,1
7	1:2	380	1,4	74,9	61,9
8	1:3	380	1,4	73,1	64,7
9	1:5	380	1,4	78,2	43,1
10	1:6	380	1,4	77,4	25,7
		Effect of rate of feed of reaction mixture			
11	1:3	380	0,5	68,9	48,1
12	1:3	380	1,0	70,2	59,3
13	1:3	380	1,4	73,1	64,7
14	1:3	380	2,0	77,7	50,3

SUMMARY

1. The catalytic condensation of 3-methyl-6-hepten-4-yn-3-ol with ammonia results in the formation of 6-ethyl-2-picoline and 2,3,6-trimethylpyridine.

2. The same products together with 2,3,5,6-tetramethylpyridine can be obtained in a total yield of 79.6% by the condensation of ammonia with a mixture of butanone and 1-buten-3-yne.

3. Reaction between ammonia, 1-buten-3-yne, and acetone gives a high yield of a readily separable mixture of 2,4,-lutidine, 2,6,-lutidine, and s-collidine.

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BUTADIYNE DERIVATIVES

COMMUNICATION 5. SYNTHESIS OF 1-ALKOXY-4-ALKYLTHIO (OR ARYLTHIO)-1,3-BUTADIENES AND THE INVESTIGATION OF VARIOUS BUTADIYNE DERIVATIVES WITH THE AID OF RAMAN SPECTRA

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In the continuation of our investigation of the properties of 1-buten-3-ynyl-ethers and sulfides prepared from butadiyne and alcohols [1] or thiols [2-4], we considered it to be of interest to determine the possibility of their reaction with alcohols and thiols. In previous investigations it was shown that 1-buten-3-ynyl ethers react with alcohols [1] and 1-buten-3-ynyl sulfides react with thiols [2-5]:

$$\underset{(I)}{CH{\equiv}C{-}CH{=}CH{-}OR} + ROH \longrightarrow CH_3{-}\underset{(II)}{C{\equiv}C{-}}CH(OR)_2 \quad (1)$$

$$\underset{(III)}{CH{\equiv}C{-}CH{=}CH{-}SR} + R'SH \longrightarrow R'S{-}\underset{(IV)}{CH{=}CH{-}CH{=}CH{-}}SR \quad (2)$$

The reaction of 1-buten-3-ynyl-ethers with alcohols proceeds by the ionic mechanism and leads to the formation of 2-butynal acetals [Equation (1)]. An attempt to carry out this reaction by the free-radical mechanism, as the present communication shows, was unsuccessful. Reaction between 1-buten-3-ynyl sulfides and thiols occurs as soon as the reactants are mixed and leads to the synthesis of symmetrical and unsymmetrical bisalkylthio (or arylthio)-1,3-butadienes [Equation (2)], the rates of formation and yields of which increase with rise in temperature and under the influence of free-radical initiators. Symmetrical bisalkylthio (or arylthio)-1,3-butadienes can be obtained also by the direct action of butadiyne on thiols [2,3].

The object of the present work was the study of the conditions for the reaction of 1-buten-3-ynyl ethers with thiols and of 1-buten-3-ynyl sulfides with alcohols, which should lead to the synthesis of various alkoxy-alkylthiobutadienes in accordance with the scheme:

$$\left.\begin{array}{l} \text{a) } CH{\equiv}C{-}CH{=}CH{-}OR + R'SH \\ \text{b) } CH{\equiv}C{-}CH{=}CH{-}SR' + ROH \end{array}\right] \longrightarrow \underset{(V)}{R'S{-}CH{=}CH{-}CH{=}CH{-}OR} \quad (3)$$

where $R' = C_2H_5$: $R = C_4H_9$ (VI); $R = C_6H_{11}$ (VII); $R = C_6H_5CH_2$ (VIII)
where $R' = C_6H_5$: $R = C_4H_9$ (IX); $R = C_6H_{11}$ (X); $R = C_6H_5CH_2$ (XI)

The investigation showed that 1-buten-3-ynyl ethers (I) react smoothly with thiols [Equation (3a)] with formation of alkoxyalkylthio (or arylthio) butadienes (V) containing alkyl, aryl, and cyclohexyl groups. It was found that benzenethiol adds to 1-buten-3-ynyl ethers on mixing of the reactants; reaction is accompanied by rise in temperature of the mixture; the presence of azobisisobutyronitrile increases the yield of products somewhat.

The addition of ethanethiol to 1-buten-3-ynyl ethers occurs more rapidly when the reactants are heated to 75-80° and the azo dinitrile is present, when a good yield of butadiene derivatives is obtained. In some cases the presence of KOH in the reaction mixture is accompanied by a lower yield of butadiene ethers, which indicates that the reaction studied proceeds more readily by the free-radical mechanism. However, attempts to bring about the addition of alcohol to the 1-buten-3-ynyl sulfide (III) [Equation (3b)] did not lead to the desired result. Under the conditions for the addition of alcohols to 1-buten-3-ynyl ethers (HCl) and under conditions favorable for the addition reactions of 1-buten-3-ynyl sulfides (azo dinitrile), alcohol did not add.

TABLE 1

Spectra of 1,4-Bisethylthio-1,3-butadiene, Prepared under the Action of KOH or the Azo Dinitrile, and of the Product Remaining after Diene Synthesis (range 2500-1300 cm^{-1})

Reagent	Product	Type of spectrum	Frequencies (cm^{-1})	
			of 1,4-bisethylthio-1,3-butadiene	other frequencies
KOH	1,4-bisethylthio-1,3-butadiene	Infrared	1592, 1544, 1495	
		Raman	1598 (600), 1543 (500), 1493	
	Residual product after diene synthesis	Infrared	1596, 1540, 1496	1948, 1702
		Raman	1600 (600), 1543 (300), 1498	1940, 1704
Azo dinitrile	1,4-bisethylthio-1,3-butadiene	Infrared	1590, 1542, 1498	
		Raman	1600 (600), 1542 (500), 1500	
	Residual product after diene synthesis	Infrared	1592, 1543, 1496	1944, 1707
		Raman	1598 (600), 1544 (300), 1498	1942, 1705

The structures of the synthesized alkoxyalkylthio (or arylthio) butadienes were proved by titration with alcoholic mercuric chloride [2], their diene condensation with maleic anhydride, and also spectroscopic investigation. In view of the fact that diene synthesis with dialkoxy- and bisalkylthio-butadienes and with the mixed butadiene ethers studied proceeds to the extent of 70-85% [2, 3], the structure of that part of the substance which does not undergo this condensation remains unexplained. In the case of bisethylthiobutadiene, spectroscopic analysis of this residual product showed that the whole of its spectrum corresponded to 1,4-bisethylthio-1,3-butadiene (Table 1), so that the incompleteness with which the diene synthesis occurs may be explained by the possible presence of cisoid and transoid configurations in the molecules of certain butadiene derivatives [5-7]. This possibility is confirmed by the fact that the intensity of the Raman line of 1540 cm^{-1} diminishes sharply as we pass from 1,4-bisethylthio-1,3-butadiene to the residual substance remaining after diene synthesis.

New lines appearing in the spectrum of the residual product may be attributed to traces of phthalic anhydride formed in the diene synthesis. Bisethylthiobutadienes synthesized by the ionic and the free-radical mechanisms were also subjected to spectroscopic analysis. In all cases the frequencies of 1,4-bisethylthio-1,3-butadienes were found (Table 1); this shows that both under ionic and under free-radical conditions the thiol adds to the 1-buten-3-ynyl sulfide at the triple bond.

EXPERIMENTAL

Synthesis of 1-Butoxy-4-(ethylthio)-1,3-butadiene (VI). A mixture of 3.4 g (0.027 mole) of 1-buten-3-ynyl butyl ether, 5.1 g (0.082 mole) of ethanethiol, and 0.025 g of azobisisobutyronitrile was heated in a sealed tube for eight hours at 75-80°. After the distillation of ethanethiol we collected the following fractions: Fraction I, b.p. 90-132° (14 mm), 0.2 g; Fraction II, 133-135° (14 mm), 4.9 g; residue 0.1 g.

After refractionation Fraction II was found to be butoxy (ethylthio)-1,3-butadiene; b.p. 102.8°(2 mm); n_D^{20} 1.5198; d_4^{20} 0.9461; Found MR 59.85. $C_{10}H_{18}SO$ 2F. Calculated MR 57.06. Found: C 64.14; 64.00; H 9.71; 9.77; S 16.69; 16.93%. $C_{10}H_{18}SO$. Calculated: C 64.47; H 9.73; S 17.21%. Yield 96.0%.

From the same amounts of reactants and 0.1 g of KOH under the same conditions we obtained 4.0 g (97.5%) of butoxy (ethylthio)-1,3-butadiene. Results on the reaction of other 1-buten-3-ynyl ethers with ethanethiol are given in Tables 2 and 4.

TABLE 2

Synthesis of Alkoxy (ethylthio)-1,3-butadienes

Original ether	Original thiol	Molar ratio ether: thiol	Reagent	Reaction temp. (°C)	Reaction time (hr)	Yield of 1,3-butadiene (%)
$CH{\equiv}C\text{-}CH{=}CH\text{-}OC_4H_9$	C_2H_5SH	1:3	Azo dinitrile	75-80	8	96.0
$CH{\equiv}C\text{-}CH{=}CH\text{-}OC_4H_9$	C_2H_5SH	1:3	KOH	75-80	8	97.5
$CH{\equiv}C\text{-}CH{=}CH\text{-}OC_6H_{11}$	C_2H_5SH	1:1	—	75-80	5	43.1
$CH{\equiv}C\text{-}CH{=}CH\text{-}OC_6H_{11}$	C_2H_5SH	1:1	KOH	75-80	6.5	72.8
$CH{\equiv}C\text{-}CH{=}CH\text{-}OC_6H_{11}$	C_2H_5SH	1:1	Azo dinitrile	75-80	6.5	92.4
$CH{\equiv}C\text{-}CH{=}CH\text{-}OCH_2C_6H_5$*	C_2H_5SH	1:1	" "	80	7.0	39.4

*Under the conditions of reaction this ether resinifies.

TABLE 3

Synthesis of Alkoxy (phenylthio)-1,3-butadienes

Original ether	Original thiol	Molar ratio ether: thiol	Reagent	Reaction temp. (°C)	Reaction time (hr)	Yield of 1,3-butadiene (%)
$CH{\equiv}C\text{-}CH{=}CHOC_4H_9$	C_6H_5SH	1:1	KOH	20-100	1.5	80.8
$CH{\equiv}C\text{-}CH{=}CHOC_6H_{11}$	C_6H_5SH	1:1	Azodinitrile	20-150	0.5	93.0
$CH{\equiv}C\text{-}CH{=}CHOCH_2C_6H_5$	C_6H_5SH	1:1	—	20-140	0.5	84.2

Synthesis of 1-(Cyclohexyloxy)-4-(phenylthio)-1,3-butadiene. A mixture of 4.6 g (0.03 mole) of 1-buten-3-ynyl cyclohexyl ether and 0.02 g of azobisisobutyronitrile was introduced into a flask fitted with stirrer and thermometer. To the stirred mixture we added 3.3 g (0.03 mole) of benzenethiol, which caused the temperature of the mixture to rise to 152°. On vacuum distillation of the mixture we collected the following fractions: Fraction I, b.p. 55-60° (2 mm), 0.2 g; Fraction II, b.p. 179-183° (2 mm), 7.35 g; residue 0.4 g.

Two distillations of Fraction II gave 1-(cyclohexyloxy)-4-(phenylthio)-1,3-butadiene; b.p. 183-183.5° (2 mm); n^{20} 1.6122; d_4^{20} 1.0663; found MR 84.91. $C_{16}H_{20}SO5F$. Calculated MR 78.97. Found: C 73.78; 73.50; H 7.68; 7.80; S 12.15; 12.20%. $C_{16}H_{20}SO$. Calculated: C 73.79; H 7.74; S 12.31%. Yield 93.0%.

Results on the reaction of other 1-buten-3-ynyl ethers with benzenethiol are given in Tables 3 and 4.

Titration of 1-(Cyclohexyloxy)-4-(phenylthio)-1,3-butadiene with Alcoholic Mercuric Chloride. To a weighed amount of the butadiene double the amount of 20% alcoholic mercuric chloride was added. The mixture was allowed to stand for two days and then titrated with 0.1 N NaOH to Methyl Orange. Found: content of the butadiene — 97.96, 98.78%.

Condensation of Butoxy (ethylthio)-1,3-butadiene (VI) with Maleic Anhydride. A mixture of 1.1 g of butoxy (ethylthio) butadiene and 0.55 g of maleic anhydride dissolved in 10 ml of benzene was heated in a sealed tube at 125-130° for ten hours. Fractionation gave 0.62 g (71.2%) of phthalic anhydride, m.p. 130-130.5°.

Reaction of 1-Buten-3-ynyl Ethyl Sulfide with Ethanol. a) In presence of HCl. A mixture of 4.0 g of 1-buten-3-ynyl ethyl sulfide [b.p. 47-48° (5 mm); n_D^{26} 1.5403] and 1.6 g of ethanol was introduced into a

TABLE 4

Characteristics of the Alkoxyethyl (or phenyl) thio-1,3-butadienes.

Formula of butadiene	Reagent in synthesis	B.p. in °C (p in mm Hg)	n_D^{20}	d_4^{20}	MR found	MR calc.	Found (%) C	Found (%) H	Found (%) S	Calculated (%) C	Calculated (%) H	Calculated (%) S
$C_6H_{11}OCH=CH-CH=CHSC_2H_5$ (VII)	Azo dinitrile	134,0 (3)	1,5468	1,0013	67,23	64,09	67,68 67,49	9,54 9,56	14,78 14,72	67,87	9,49	15,09
The same	KOH	136—137 (3)	1,5460	—	—	—	—	—	—	—	—	—
$C_6H_5CH_2O-CH=CH-CH=CH-SC_2H_5$ (VIII)	Azo dinitrile	148—148,5 (2,5)	1,5755	1,0122	71,98	67,31	70,95 71,05	7,57 7,53	14,65 14,65	70,87	7,32	14,55
$C_4H_9O-CH=CH-CH=CH-SC_6H_5$	KOH	153—153,5 (2)	1,5929	1,0261	77,38	71,93	71,55 71,30	7,75 7,79	13,35 13,40	71,75	7,74	13,68
$C_6H_{11}O-CH=CH-CH=CH-SC_6H_5$ (X)	Azo dinitrile	183—183,5 (2)	1,6122	1,0863	84,91	78,97	73,78 73,50	7,68 7,80	12,15 12,20	73,79	7,74	12,31
$C_6H_5CH_2O-CH=CH-CH=CH-SC_6H_5$ (XI)	—	203 (3,5)	1,6184	1,1196	84,03	82,18	76,04 76,05	6,14 6,11	11,96 11,98	76,08	6,01	11,95

three-necked flask fitted with stirrer and thermometer, and with stirring we added two drops of concentrated hydrochloric acid. Stirring was continued for four hours, after which the acid was neutralized with sodium carbonate and the product was fractionated. We isolated 3.5 g of 1-buten-3-ynyl ethyl sulfide; b.p. 46-47° (5 mm); n_D^{26} 1.5402.

b) In presence of azobisisobutyronitrile. A mixture of 2 g of 1-buten-3-ynyl ethyl sulfide, 3 g of ethanol, and 0.01 g of azobisisobutyronitrile was heated in a sealed tube for six hours at 65-70°. After fractionation we isolated 1.8 g of unchanged 1-buten-3-ynyl ethyl sulfide; b.p. 53° (8.5 mm); n_D^{20} 1.5450.

Reaction of 1-Buten-3-ynyl Butyl Ether with Butyl Alcohol in Presence of the Azo Dinitrile. a) A mixture of 3.4 g of 1-buten-3-ynyl butyl ether [b.p. 54-55° (8 mm); n_D^{20} 1.7402], 6.2 g of butyl alcohol, and 0.03 g of azobisisobutyronitrile was heated in a sealed tube at 100-110° for 7.5 hours. After fractionation of the contents of the tube we isolated 6.3 g of butyl alcohol, 2.95 g of 1-buten-3-ynyl butyl ether [b.p. 53-54° (7 mm); n_D^{20} 1.4700] and 0.3 g of resin.

Spectroscopic Investigations. Five main types of butadiyne derivatives, synthesized by us [1-3], were subjected to spectroscopic investigation: 1-buten-3-ynyl ethers [1], 1-buten-3-ynyl sulfides [3], butynal acetals [2], 1,4-bisalkyl (or phenyl) thio-1,3-butadienes [4], and 1-alkoxy-4-alkyl (or phenyl) thio-1,3-butadienes. The infrared and Raman spectra of these compounds were studied. The infrared absorption spectra of these compounds were determined with a single-beam IKS-11 infrared spectrometer with a layer thickness of 0.05 mm. The spectrum range 1400-2500 cm^{-1} was studied. The results are summarized in Table 5. The error in frequency determination depends on the region of the spectrum and is in the range 5-10 cm^{-1}.

The Raman spectra were determined with the object of measuring the frequencies of certain vibrations with greater accuracy (the error in the measurement of frequency did not exceed 2 cm^{-1}). The Raman spectra were determined in a standard ISP-51 apparatus in cyclohexane solutions; the concentrations were low, because the compounds investigated were appreciably colored. The exposure was limited by the decomposition of the substance under the action of radiation and did not exceed one hour. This explains the incompleteness of some spectra. The results of measurements on the Raman spectra are shown in Table 6.

The numbers in parentheses in Table 6 are integral intensity coefficients estimated visually on a scale on which the unit is one-hundredth of the intensity of the 313 cm^{-1} line, calculated for 1 M (excitation by the blue mercury line).

TABLE 5

Infrared Spectra of Substances Investigated *

Formula	Vibration frequencies (cm^{-1}) of				
	C≡C	C=C	benzene ring	C–H	C=O
$CH\equiv C-CH=CH-OC_4H_9$	2096 ср	1632 и		1456 и	1772 сл
$CH\equiv C-CH=CH-OC_6H_{11}$	2092 ср	1634 и		1470 и	
$CH\equiv C-CH=CH-OCH_2C_6H_5$	2094 ср	1635 и	1944 сл 1588 и 1472 и	1450 и	1704 ср
$CH\equiv C-CH=CH-SC_2H_5$	2090 ср	1566 и		1444 и	
$CH\equiv C-CH=CH-SC_6H_5$	2094 ср	1574 и	1934 сл 1583 и 1474 и	1438 и	
$CH_3-C\equiv C-CH-(OCH_2C_6H_5)_2$	2235 сл		1942 ср 1596 и 1478 и	1454 и	1700 ср
$C_2H_5S-CH=CH-CH=CH-SC_2H_5$		1592 ср 1542 и		1496 и	
$C_6H_5-S-CH=CH-CH=CH-SC_6H_5$		1660 ср 1602 и	1942 ср 1590 и 1470 и	1470 и	
$C_2H_5S-CH=CH-CH=CH-SC_6H_5$		1650 ср 1586 и	1934 сл 1594 и 1470 и	1440 и	
$C_2H_5S-CH=CH-CH=CH-OC_4H_9$		1644 и 1575 и		1450 и	1774 сл
$C_6H_5S-CH=CH-CH=CH-OC_4H_9$		1658 и 1594 и	1936 сл 1574 и 1472 и	1472 и	1774 сл
$C_6H_5S-CH=CH-CH=CH-OC_6H_{11}$		1650 и 1592 и	1934 сл 1572 и 1472 и	1472 и	
$C_6H_5S-CH=CH-CH=CH-OCH_2C_6H_5$		1655 ср 1594 и	1938 ср 1580 и 1474 и	1446 и	1702 ср
$C_2H_5S-CH=CH-CH=CH-OC_6H_{11}$		1638 и 1574 и		1446 и	1774 сл
$C_2H_5S-CH=CH-CH=CH-OCH_2C_6H_5$		1640 ср 1570 ср	1945 сл 1594 и 1469 и	1469 и	1703 ср

*Intensities are indicated on a three-grade scale: и – intense; ср – of medium intensity; сл – weak.

TABLE 6

Raman Spectra of the Compounds Investigated

$CH\equiv C-CH=CH-OC_4H_9$	$CH\equiv C-CH=CH-SC_2H_5$	$C_2H_5S-CH=CH-CH=CH-OC_4H_9$	$C_2H_5S-CH=CH-CH=CH-OC_6H_{11}$	$C_2H_5S-CH=CH-CH=CH-SC_2H_5$
321 (background)				
510 (100)				
				699 (0)
				783 (20)
915 (50)			835 (100)	847 (0)
1032 (0)				863 (10)
1070 (0)				1050 (20)
				1088 (20)
1228 (10)	1215 (20)		1135 (50)	1134 (20)
1268 (10 dble)				1189 (50)
1315 (10 dble)			1212 (100)	
1412 (20)			1240 (50)	1236 (100)
1452 (10)			1294 (50)	1291 (50)
1472 (20)			1442 (50)	
				1493 (50)
1631 (500)	1563 (500)	1576 (500)	1573 (500)	1543 (500)
2099 (400)	2099 (400)	1642 (600)	1638 (600)	1600 (600)

As will be seen from the spectra (Tables 5 and 6), the triple C ≡ C bond interacts strongly with the double C = C bond. The mutual effect of these is manifest in some lowering of frequencies and increase in intensities of the corresponding infrared absorption bands and Raman lines [8, 9].

It is interesting that for 1-buten-3-ynyl ethers and sulfides the C = C double bond frequency is not split, as it is in the case of various vinyl ethers and sulfides [10]. This fact is evidently to be explained by the presence of only one of the conceivable configurations for rotational isomers. The effect of the hetero atom in the molecules of the type $C \equiv C-C=C-X$ ($X = OC_4H_9$, OC_6H_{11}, $OCH_2C_6H_5$, SC_2H_5, SC_6H_5) is shown in the value of the double bond frequency: for sulfides it is lowered to a much greater extent than for ethers. An analogous effect has been observed also by other authors [11]. The triple C≡C bond is probably not greatly affected by hetero atoms, and its frequency is the same for ethers, sulfides, and 1-buten-3-yne [9]. In this case, evidently, the screening effect of the double C=C bond is operative. Actually, as shown in [12], the mutual effect of groups of atoms separated by π-bond systems weakens as these systems are lengthened.

TABLE 7

Dependence of C=C Vibration Frequencies on Presence of Hetero Atoms and Groups

Compound	Frequencies (cm^{-1})	
$H_5C_2S-CH=CH-CH=CH-SC_2H_5$	1600	1540
$H_5C_6S-CH=CH-CH=CH-SC_2H_5$	1650	1585
$H_5C_6S-CH=CH-CH=CH-SC_6H_5$	1660	1600
$H_5C_2S-CH=CH-CH=CH-OR$	1640	1575
$H_5C_6S-CH=CH-CH=CH-OR$	1655	1595

Note: R = C_4H_9; C_6H_{11}; $CH_2C_6H_5$.

The substituted butadiene molecules that we investigated contained two conjugated C=C double bonds. In the spectra of these molecules the double bond frequency is split into two components, which are separated by about 60 cm^{-1}. The splitting of the C=C double bond frequency may be most readily explained by the presence of rotational isomers.

The C=C frequency in compounds of the type $X-C=C-C=C-Y$ (in which X and Y = OC_4H_9, OC_6H_{11}, $OCH_2C_6H_5$, SC_2H_5, SC_6H_5) depends on the natures of the hetero atoms and groups present. This relation is seen from Table 7.

SUMMARY

1. The conditions were found for the synthesis of 1-alkoxy-4-alkylthio (or arylthio)-1,3-butadienes from 1-buten-3-ynyl ethers and thiols in good yield. Their structures were proved by titration with alcoholic mercuric chloride, the results of their diene condensation, and spectrum analysis.

2. A study was made of the infrared and Raman spectra of the main functional derivatives of butadiyne synthesized by the authors: 1-buten-3-ynyl ethers and sulfides, 2-butynal acetals, bisalkylthio (or phenylthio)-1,3-butadienes, and 1-alkoxy-4-alkylthio (or phenylthio)-1,3-butadienes. The mutual effects of multiple bonds, hetero atoms, and groups in the molecules of the compounds investigated were noted.

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*Original Russian pagination. See C. B. translation.

**As in the Russian original.

VINYL COMPOUNDS IN DIENE SYNTHESIS

COMMUNICATION 3. SYNTHESIS AND PROPERTIES OF ETHERS OF THE 2-NORBORNENE AND OCTAHYDRODIMETHANONAPHTHALENE SERIES CONTAINING AROMATIC GROUPS

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July, 1960,
Original article submitted December 29, 1958

Of the vinyl ethers investigated in diene condensations with cyclopentadiene and hexachlorocyclopentadiene, those containing aromatic groups are among the most active.

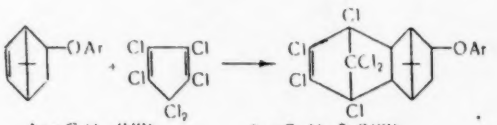
In continuation of our systematic investigation of diene condensations with vinyl compounds of the type $CH_2 = CH - XR$ [1,2], we studied the reactions of cyclopentadiene and of hexachlorocyclopentadiene with the following aryl vinyl ethers: 2-naphthyl vinyl, phenyl vinyl, and p-t-butylphenyl vinyl.

The condensation of aryl vinyl ethers with cyclopentadiene results in the formation of the corresponding ethers of 2-norbornene [bicyclo[2.2.1]hept-2-ene] and 1,2,3,4,4a,5,8,8a-octahydro-1,4:5,8-dimethanonaphthalene:

Ar = C_6H_5 (I) Ar = C_6H_5 (IV)
Ar = $C_6H_4C_4H_9$-t (II) Ar = $C_6H_4C_4H_9$-t (V)
Ar = $C_{10}H_7$-β (III) Ar = $C_{10}H_7$-β (VI)

(1)

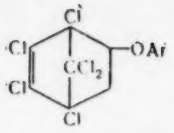
The relative amounts of the adducts formed [e.g., (I) and (IV)] can be regulated by adjusting the relative amounts of the reactants. As stated previously, for alkyl vinyl ethers [1], as also in the present case, the second stage of this reaction may be carried out with hexachlorocyclopentadiene with formation of ethers of dihydroaldrin [ethers of 5,6,7,8,9,9-hexachloro-1,2,3,4,4a,5,8,8a-octahydro-1,4:5,8-dimethanonaphthalene]:



Ar = C_6H_5 (VII) Ar = $C_{10}H_7$-β (VIII)

(2)

The condensation of aryl vinyl ethers with hexachlorocyclopentadiene leads to the formation of ethers of hexachloro-2-norbornene:

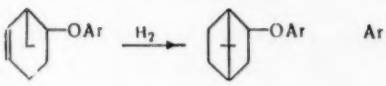


Ar = C_6H_5 (IX)
Ar = $C_6H_4C_4H_9$-t (X)
Ar = $C_{10}H_7$-β (XI)

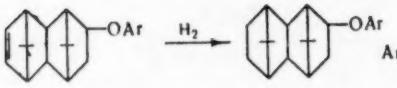
For the characterization of adducts prepared from cyclopentadiene, use is generally made of the double bond of 2-norbornene, since it is known that a double bond in bicycles having a methylene bridge has enhanced activity. Reactions suitable for this purpose are hydrogenation and reaction with phenyl azide. Hydrogenation of the double bond of the 2-norbornene system proceeds smoothly over the usual hydrogenation catalysts and leads to the corresponding saturated compounds [3-5].

The reaction of 2-norbornene derivatives with phenyl azide was first carried out by Alder and Stein [6]. These authors found that the double bond in strained ring systems of the 2-norbornene type is extremely sensitive toward phenyl azide, whereas the double bond in unstrained cycles of the cylohexene and bicyclo[2.2.2]octene types does not react with phenyl azide under the same conditions. On this basis the authors concluded that the readiness with which reaction occurs between diene-synthesis adducts and phenyl azide may serve as a criterion of the 2-norbornene structure, and this has been confirmed several times in other work [7, 8].

For the characterization of the derivatives of 2-norbornene and octahydrodimethanonaphthalene [Equation (1)] prepared from aryl vinyl ethers, use was made of the reactions described above. Hydrogenation of the adducts over platinum oxide at room temperature led to the isolation of saturated ethers of norbornane[(Equation (3)] and decahydrodimethanonaphthalene [Equation (4)] in high yields:

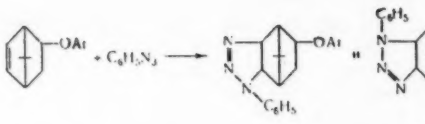


Ar = C_6H_5 (XII); $C_6H_4C_4H_9$-t (XIII); $C_{10}H_7$-β (XIV) (3)

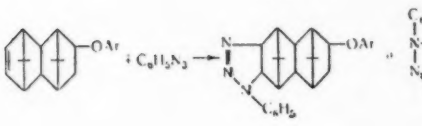


Ar = C_6H_5 (XV); $C_6H_4C_4H_9$-t (XVI); $C_{10}H_7$-β (XVII) (4)

The hydrogenated adducts were viscous liquids or crystalline substances with a camphorlike odor. As would be expected, the reaction of the synthesized adducts with phenyl azide proceeded smoothly under mild conditions and resulted in the formation of crystalline derivatives of dihydrotriazole, probably in the form of mixtures of isomers [9]:



Ar = C_6H_5 (XVIII); $C_6H_4C_4H_9$ (XIX) (5)



Ar = C_6H_5 (XX); $C_6H_4C_4H_9$ (XXI); $C_{10}H_7$ (XXII) (5)

EXPERIMENTAL

Reaction of 2-Naphthyl Vinyl Ether with Cyclopentadiene [Equation (1)]. a) Ratio 2 : 1. A mixture of 34 g (0.2 mole) of 2-naphthyl vinyl ether and 6.6 g (0.05 mole) of cyclopentadiene dimer was prepared in a 200-ml autoclave. The mixture was heated at 170° for 14 hours, and the pressure in the autoclave did not exceed 3-4 atm. The viscous dark-yellow product was vacuum-fractionated: Fraction I, b.p. 100-102° (3 mm), n_D^{20} 1.6145, 25.9 g; Fraction II, b.p. 102-152° (3 mm), n_D^{20} 1.6115, 0.3 g; Fraction III, b.p. 155-160° (3 mm), n_D^{20} 1.6153, 8.5 g; residue 4.5 g.

Fractions I and II contained unchanged naphthyl vinyl ether. From Fraction III, after repeated fractionation, we isolated 5-(2-naphthyloxy)-2-norbornene (III) as a thick colorless liquid with an odor of camphor; b.p. 154-154.5° (2.5 mm); n_D^{20} 1.6162. After it had stood for a short time the adduct crystallized out in gleaming needles, m.p. 65.5-67° (from methanol). Found: C 86.32; 86.28; H 6.95; 6.96%. $C_{17}H_{16}O$. Calculated: C 86.40; H 6.83%. Yield 72.3%.

From the residue we isolated 2.1 g of a product of b.p. 170-172° (0.006 mm), which rapidly solidified to a white amorphous material and was found to be 1,2,3,4,4a,5,8,8a-octahydro-2-(2-naphthyloxy)-1,4:5,8-dimethanonaphthalene (VI). Found: C 86.92; 86.73; H 7.16; 6.97%. $C_{22}H_{22}O$. Calculated: C 87.36; H 7.33%. Yield 14.6%.

b) Ratio 1 : 1. Under similar conditions from a mixture of 34 g (0.2 mole) of 2-naphthyl vinyl ether and 13.2 g (0.1 mole) of cyclopentadiene dimer we obtained 12.9 g (67.1%) of 5-(2-naphthyloxy)-2-norbornene (III) and 7.5 g (30.6%) of 1,2,3,4,4a,5,8,8a-octahydro-2-(2-naphthyloxy)-1,4:5,8-dimethanonaphthalene (VI).

Reaction of p-t-Butylphenyl Vinyl Ether with Cyclopentadiene. From a mixture of 49.6 g (0.3 mole) of p-t-butylphenyl vinyl ether and 13.2 g (0.2 mole) of cyclopentadiene, treated under the above-described conditions, we obtained 34.6 g of unchanged vinyl ether and two reaction products: 1) 12.85 g (62.3%) of 5-p-t-butylphenoxy-2-norbornene (II), as gleaming white needles (from methanol), m.p. 35-36° and b.p. 135-135.5° (1.5 mm) (Found: C 84.29; 84.58; H 9.25; 8.88%. $C_{17}H_{22}O$. Calculated: C 84.24; H 9.15%); 2) 8.7 g (33.2%) of 1,2,3,4,4a,5,8,8a-octahydro-2-p-t-butylphenoxy-1,4:5,8-dimethanonaphthalene (V), b.p. 193-193.5° (2 mm), as a colorless glassy mass (Found: C 85.55; 85.39; H 9.03; 8.92%. $C_{22}H_{28}O$. Calculated: C 85.65; H 8.97%).

Synthesis of 1,2,3,4,7,7-Hexachloro-5-(2-naphthyloxy)-2-norbornene (XI). A mixture of 3.4 g (0.02 mole) of 2-naphthyl vinyl ether and 5.4 g (0.02 mole) of hexachloropentadiene was heated in a small flask under reflux at 110-120° for 3.5 hours. After removal of unchanged hexachlorocyclopentadiene (1.2 g) and 2-naphthyl vinyl ether (0.5 g), we isolated a fraction (5.0 g) of b.p. 205-215° (2 mm), which solidified on standing: this gave 1,2,3,4,7,7-hexachloro-5-(2-naphthyloxy)-2-norbornene (XI) in the form of gleaming white crystals. After recrystallization from benzene-methanol mixture, the substance had m.p. 112-113° and b.p. 204-206° (1 mm). Found: C 46.36; 46.39; H 2.46; 2.50; Cl 48.38; 48.31%. $C_{17}H_{10}Cl_6O$. Calculated: C 46.09; H 2.50; Cl 48.03%. Yield 56.8%.

Under similar conditions, from 5.2 g of p-t-butylphenyl vinyl ether and 5.4 g of hexachlorocyclopentadiene we obtained 5.0 g (61.4%) of 1,2,3,4,7,7-hexachloro-5-p-t-butylphenoxy-2-norbornene (X), which had the following constants: b.p. 199-202° (2 mm); b.p. 81-82° (from methanol). Found: C 45.48; 45.66; H 3.60; 3.70; Cl 47.72; 47.67%. $C_{17}H_{16}Cl_6O$. Calculated: C 45.46; H 3.59; Cl 47.39%.

Similarly, from 3.6 g (0.03 mole) of phenyl vinyl ether and 8.1 g (0.03 mole) of hexachloropentadiene we obtained 8.9 g (90.8%) of 1,2,3,4,7,7-hexachloro-5-phenoxy-2-norbornene (IX), a pale-yellow liquid, b.p. 161° (3 mm) and n_D^{20} 1.5800. Found: C 39.97; 39.92; H 2.02; 2.09; Cl 54.02; 54.19%. $C_{13}H_8Cl_6O$. Calculated: C 39.72; H 2.05; Cl 54.14%.

Synthesis of 2-Naphthyloxy Dihydroaldrin (VIII). A mixture of 3.6 g (0.015 mole) of 5-(2-naphthyloxy)-2-norbornene (III) and 4.1 g (0.015 mole) of hexachlorocyclopentadiene was heated under reflux at 120-135° for 5.5 hours. Unchanged reactants (3.6 g) were vacuum-distilled from the product. The residue was treated with p-xylene to remove the resin formed and was crystallized from a benzene-methanol mixture. We isolated 3.5 g (74.4%) of 5,6,7,8,9,9-hexachloro-1,2,3,4,4a,5,8,8a-octahydro-2-(2-naphthyloxy)-1,4:5,8-dimethanonaphthalene (naphthyloxy aldrin) (VIII), m.p. 110-111° and b.p. 198-200° ($4.6 \cdot 10^{-3}$ mm). Found: C 52.00; 52.14; H 3.11; 3.24; Cl 41.50; 41.25%. $C_{22}H_{16}Cl_6O$. Calculated: C 51.89; H 3.17; Cl 41.78%.

TABLE 1

Name of original ether	Solvent	Yield of hydrogenation product (%)
5-(2-naphthyloxy)-2-norbornene (III)	Methanol + Ether	81.2 (XIV)
1,2,3,4,4a,5,8,8a-octahydro-2-(2-naphthyloxy)-1,4:5,8-dimethanonaphthalene (VI)	Dioxane	80.0 (XVII)
1,2,3,4,4a,5,8,8a-octahydro-2-phenoxy-1,4:5,8-dimethanonaphthalene (IV)	Methanol + Ether	81.4 (XV)
5-p-t-butylphenoxy-2-norbornene (II)	Dioxane	95 (XIII)
1,2,3,4,4a,5,8,8a-octahydro-2-(p-t-butylphenoxy)-1,4:5,8-dimethanonaphthalene (V)	"	92.3 (XVI)

Hydrogenation of 5-Phenoxy-2-norbornene [Equation (3)]. 5-Phenoxy-2-norbornene (I) (2 g) was hydrogenated in methanol (20 ml) in a long-necked flask over Adams platinum oxide. The volume of hydrogen absorbed at room temperature during 45 minutes was 235 ml (the theoretical amount was 240 ml). After removal of methanol the hydrogenation product was vacuum-fractionated. We isolated 1.7 g (87.6%) of 2-phenoxynorbornane (XII); b.p. 98° (1 mm); n_D^{20} 1.5350; d_4^{20} 1.0482; found MR 55.94; $C_{13}H_{16}O3F$. Calculated MR 55.88. Found: C 83.08; 83.04; H 8.52; 9.03%. $C_{13}H_{16}O$. Calculated: C 82.88; H 8.57%.

The results of experiments on the hydrogenation of the other ethers are given in Table 1.

The constants and analyses of the hydrogenated adducts are given in Table 2.

TABLE 2

Hydrogenated ether	b.p. in °C (p in mm)	n_D^{20}	Found (%)		Calculated (%)	
			C	H	C	H
2-(2-Naphthyloxy)norbornane (XIV)	166-167 (3)	1.6012	85.75	7.58	85.67	7.61
Decahydro-2-(2-naphthyloxy)-1,4:5,8-dimethanonaphthalene (XVII)	215-216 (2)	Solid	85.66 86.67	7.65 7.91	86.78	7.95
Decahydro-2-phenoxy-1,4:5,8-dimethanonaphthalene (XV)	183-184 (2)	1.5623	86.67 84.82	8.02 8.78	85.00	8.72
2-p-t-butylphenoxynorbornane (XIII)	133-133.5 (2)	1.5265	84.64 83.24	8.78 10.00	83.54	9.90
Decahydro-2-p-t-butylphenoxy-1,4:5,8-dimethanonaphthalene (XVI)	217-218 (4)	Solid	84.76 84.73	9.56 9.57	85.07	9.76

Preparation of Dihydrotriazole Derivatives from the Adducts Isolated. A mixture of 0.7 g of 1,2,3,4,4a,5,8,8a-octahydro-2-(2-naphthyloxy)-1,4:5,8-dimethanonaphthalene (VI) and 2 g of phenyl azide was set aside at room temperature. Crystallization was observed after two days. The mixture was left further for five days, after which the precipitate was separated and recrystallized from ethyl acetate. The resulting dihydrotriazole (XXII) had m.p. 213-214° (decomp.). Found: C 79.88; 79.72; H 6.59; 6.52; N 9.78; 9.69%. $C_{28}H_{27}N_3O$. Calculated: C 79.79; H 6.46; N 9.97%.

In a similar way dihydrotriazole derivatives were prepared by the condensation of phenylazide with other adducts:

1) 5-Phenoxy-2-norbornene (I) gave the dihydrotriazole (XVIII), m.p. 135-137.5° (decomp.). Found: N 13.89; 13.81%. Calculated: N 13.76%.

2) 5-p-t-Butylphenoxy-2-norbornene (II) gave the dihydrotriazole (XIX), m.p. 165.5-167° (decomp.). Found: N 11.85; 12.07%. Calculated: N 11.62%.

3) 1,2,3,4,4a,5,8,8a-Octahydro-2-phenoxy-1,4:5,8-dimethanonaphthalene (IV) gave the dihydrotriazole (XX), m.p. 190.5-191.5° (decomp.). Found: N 11.48; 11.50%. Calculated: N 11.31%.

4) 1,2,3,4,4a,5,8,8a-Octahydro-2-(p-t-butylphenoxy)-1,4:5,8-dimethanonaphthalene (V) gave the dihydrotriazole (XXI), m.p. 198-200° (decomp.). Found: N 9.73; 9.79%. Calculated: N 9.83%.

SUMMARY

1. The diene condensations of 2-naphthyl vinyl ether and of p-t-butylphenyl vinyl ether with cyclopentadiene and with hexachlorocyclopentadiene were carried out.

2. Good yields were obtained of aromatic ethers of 2-norbornene, octahydrodimethanonaphthalene, hexachloro-2-norbornene, and dihydroaldrin. The adducts formed with cyclopentadiene were hydrogenated to the corresponding derivatives of norbornane and decahydrodimethanonaphthalene, and crystalline derivatives formed with phenyl azide were prepared.

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*Original Russian pagination. See C. B. translation.

CATALYTIC POLYMERIZATION OF OLEFINS

COMMUNICATION 11. EFFECT OF FOREIGN SUBSTANCES IN THE ORIGINAL GAS AND OF THE MATERIAL OF THE WALLS OF THE REACTION VESSEL ON THE COURSE OF THE POLYMERIZATION OF ETHYLENE OVER NICKEL CATALYSTS

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July, 1960,
Original article submitted November 12, 1958

In the preceding communication [1] we described the effect of temperature and time of contact on the course of the polymerization of ethylene over nickel catalysts [2]. The object of the present work was the investigation of the effect of foreign substances in the original ethylene, the effect of treatment of the catalyst with various substances, and finally the effect of the nature of the material of the reaction tube on the course of this reaction. The experimental procedure remained as before [1, 2].

EXPERIMENTAL

Effect of Foreign Substances in the Original Ethylene and Effect of Treatment of the Catalyst with Various Substances on its Activity. The questions of the effect of foreign substances in the original ethylene and of the effect of treatment of the catalyst with various substances on its activity are closely related. It was already clear from previous experiments that the activity of the catalyst used in the polymerization of ethylene rapidly falls with time. Simultaneously the catalyst becomes covered with carbonaceous deposits. It was previously shown [1] that in the passage of ethylene over the catalyst at 100-150°, at which temperatures the polymerization of ethylene scarcely goes at all, the catalyst is nevertheless poisoned, and at a higher temperature it has a lower activity than a freshly prepared or regenerated catalyst at the same temperature. It is probable that ethylene itself, or its polymerization products, can already undergo decomposition or condensation with formation of substances that block the active centers of the surface. By extraction of a spent catalyst with organic solvents (acetone and benzene), we succeeded in extracting 5-8% (on the weight of the catalyst) of macromolecular resinous substances from the catalyst. However, after this treatment the catalyst does not become more active. Only after the carbonaceous deposit has been roasted in a stream of air at 450° for 1-3 hours is the activity of the catalyst recovered to an appreciable extent. It was natural to expect that when the original ethylene contains an admixture of its homologs, which may be decomposed more readily than ethylene itself under the conditions of reaction, poisoning of the catalyst may occur still more rapidly, which should cause a reduction in activity. The correctness of this view was confirmed in experiments with ethylene to which propene, butene, or butane had been added. The experiments lasted 5-6 hours and were carried out at 275° with a time of contact of 2.3 seconds. The catalysts used were samples of a nitrate-impregnation NiO catalyst with a finely spherical aluminum silicate as carrier. The catalyst was regenerated after each six-hour experiment in a stream of air at 450° for two hours.

TABLE 1

Catalyst	Experiment	Propene content of original ethylene (%)	Yield of butene (%)		Yield of higher hydrocarbons (%)	
			on ethylene passed	on ethylene that reacts	on ethylene passed	on ethylene that reacts
336	1	0,0	20,8	79,0	5,4	20,7
336	2	0,5	22,6	77,0	4,2	18,6
336	3	0,0	22,6	79,6	5,8	20,4
314	1	0,0	14,2	74,2	1,6	8,1
314	2	3,0	19,3	87,2	2,9	13,8
314	3	0,0	19,3	79,0	4,0	16,0
335	1	0,0	31,3	62,5	10,0	20,3
335	2	5,0	20,0	67,0	9,3	33,0
335	3	5,0	13,7	56,2	3,6	15,9
335	4	0,0	16,6	82,0	3,7	18,0

TABLE 2

Catalyst	Experiment	Butene content of original ethylene (%)	Yield of butene (%)		Yield of higher hydrocarbons (%)	
			on ethylene passed	on ethylene that reacts	on ethylene passed	on ethylene that reacts
312	1	0,0	41,4	84,6	7,2	14,2
312	2	3,0	30,0	82,6	3,5	9,7
312	3	0,0	25,9	67,0	3,5	9,0
312	4	5,5	10,1	65,0	2,3	15,1
312	5	0,0	17,1	78,5	2,3	10,5
313	1	0,0	24,4	78,2	6,9	22,3
313	2	10,0	16,2	69,2	5,8	24,1
313	3	0,0	19,1	83,6	1,5	19,8
313	4	3,0	14,0	67,0	2,4	12,0

Table 1 gives the results of experiments with ethylene containing 0.5-5.0% of propene. As will be seen from data on the work of Catalysts 336 and 314, the addition of 0.5-3% of propene does not result in any particular lowering of activity and selectivity (with respect to dimerization) of the catalyst. However, from data on the work of Catalyst 335 it is seen that the addition of 5% propene to the ethylene already has a deactivating effect on the catalyst: the activity falls, and then also the selectivity. This poisoning has a reversible character and on subsequent passage of pure ethylene the activity and selectivity are recovered. Table 2 shows that the admixture of butene has a similar effect.

Investigation of the effect of the addition of hydrogen to the original ethylene and also of prior treatment of the NiO-aluminum silicate with hydrogen showed that in both cases the activity of the catalyst is affected adversely. Catalyst 136, which was used in these experiments, was a formate-impregnation catalyst on aluminum silicate in tablet form and it was given a preliminary roasting in a stream of hydrogen at 300° for one hour. At 300° with a time of contact of 12 seconds and with ethylene containing 3-6% of hydrogen, we obtained a yield of dimer of 37.0-23.0% on the amount of ethylene passed and 46.5-50.8% on the amount that reacted. In absence of hydrogen the yields were 41.0-23.6% and 58.8-43.5%, respectively. When the hydrogen content of the original gas was 30-40%, polymerization was retarded.

To investigate the effect of water vapor on the reaction, the original ethylene was passed through a flask containing water heated to 70-90°. In these experiments we studied the work of Catalysts 139, 140, and 144, which were prepared as formate-impregnation catalysts with a carrier of aluminum silicate in tablet form. Table 3 and Fig. 1 give results on the work of these catalysts at 300°, and for comparison we give data on the work of an analogous catalyst (Catalyst 77), but with water-free ethylene. The results show that addition of water vapor to the original ethylene leads to deactivation of the catalyst and loss of catalytic stability.

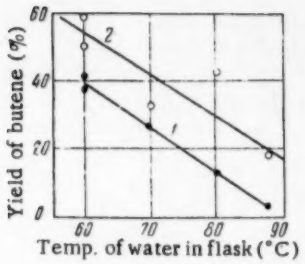

Fig. 1. Effect of the presence of water vapor in the original ethylene on the course of the polymerization of ethylene: 1) yield of butene (% on ethylene passed), 2) yield of butene (% on ethylene that reacted).

Effect of Material of Reaction Tube. Until now we have carried out the catalytic polymerization of ethylene over nickel catalysts in a glass reaction tube. In the present work, to study the effect of the material of the reaction tube, we have used tubes of stainless steel, brass, and, for comparison, glass of diameter 10 mm and stainless steel of diameter 18 mm. The experiments were carried out at atmospheric pressure, at a temperature of 275°, and with a time of contact of 2-4 seconds. We used a nitrate-impregnation NiO-aluminum silicate catalyst [1], all samples of which were prepared from the same reagents under the same conditions and on the same carrier, for which we used finely spherical aluminum silicate of grain size 0.2 mm. After 5-6 hours the work of the catalyst was interrupted for 12 hours. Before the catalyst was put into work, and also after every interruption, the catalyst was treated with air at 450° for two hours. The results of the experiments are given in Table 4, which gives the average yields of butene and higher polymers on the amounts of ethylene passed and ethylene that reacted for the whole period of work of each sample of catalyst. It will be seen that these average yields depend on the duration of work of the catalyst. This relation varies in character for tubes of different materials. It is noteworthy that, in a glass tube, the yield of butene on the ethylene passed does not change with change in the duration of the work of the catalyst and is equal to 20%. This indicates that under the given conditions the catalyst has good regenerability. The same is observed in work with a brass tube, for which the yield of butene is somewhat higher and equal to 23-25%. In steel tubes the initial activity of the catalyst is somewhat higher and the yield of butene on the ethylene passed is higher and equal to 28-35%. However, in these tubes the catalyst does not show such a good regenerability as in glass and brass tubes, and in experiments of 24 hours duration the yield of butene falls to 18-20%. In all the tubes the yield of butene on the ethylene that reacted was 65-73%. The nature of the material of the tube has no particular effect on the yield of higher hydrocarbons, which was 5-11% on the ethylene passed and 18-24% on the ethylene that reacted.

TABLE 3

Catalyst	Temperature of water in flask (°C)	Expt. No.	Time of contact (sec)	Yield of butene (%)		Yield of higher hydrocarbons (%)	
				on ethylene passed	on ethylene that reacts	on ethylene passed	on ethylene that reacts
77	—	1	12	41,0	58,8	26,7	34,8
77	—	2	12	38,8	50,5	14,8	21,3
139	70—75	1	7	26,7	33,0	15,9	19,6
139	70—75	2	10	5,4	36,0	2,1	14,0
144	80	1	5	13,9	44,0	5,1	16,2
144	80	2	5	0,0	0,0	0,0	0,0
140	90	1	11	2,5	19,0	2,0	15,4
140	90	2	10	3,3	20,0	1,5	9,2

Table 5 gives results obtained in prolonged experiments (up to 105 hours) in a stainless steel tube, 10 mm in diameter. In these experiments the average yield of butene in 20 hours of work was about 24%. For more prolonged work this yield gradually fell, and by 105 hours it had fallen to 16.6%. The yield of butene on the amount of ethylene that reacted remained at 68-70%. The yield of higher hydrocarbons was 5-6% on the ethylene passed and 20-21% on the ethylene that reacted.

SUMMARY

1. The addition to ethylene of propene and butene (more than 3%), and also of hydrogen and water vapor, greatly lowers the activity and selectivity of nickel catalysts for the polymerization of ethylene.

2. When the reaction is carried out in brass and glass tubes, the catalyst is readily regenerable, but in steel tubes the regenerability falls as reaction is prolonged. The nature of the material of the reactor does not affect the selectivity of the catalyst.

TABLE 4

Portion of catalyst	Material of tube	Diameter of tube in mm	Duration of catalyst action (hr)	Yield of butene (%)		Yield of higher hydrocarbons (%)	
				on ethylene passed	on ethylene that reacts	on ethylene passed	on ethylene that reacts
1	Stainless steel	10	6	34,7	72,1	11,7	24,2
2	" " "	10	12	26,0	71,9	6,6	22,8
3	" " "	10	18	22,7	69,0	7,3	22,1
4	" " "	10	24	17,8	64,7	5,3	19,6
5	" " "	18	6	27,8	69,5	18,6	21,6
6	" " "	18	12	24,0	74,0	11,2	22,1
7	" " "	18	18	20,8	70,7	8,7	19,5
8	" " "	18	24	19,7	71,0	7,9	19,7
9	Brass	10	6	23,1	69,5	6,5	17,8
10	" "	10	12	25,7	72,7	8,0	21,7
11	" "	10	18	25,0	71,5	8,2	22,9
12	" "	10	24	24,5	70,7	7,5	21,3
13	Glass	10	6	20,5	71,2	6,0	20,0
14	" "	10	18	20,4	71,0	5,6	18,8
15	" "	10	24	20,9	65,5	6,1	18,5

TABLE 5

Portion of catalyst	Duration of action in hr	Yield of butene (%)		Yield of higher hydrocarbons (%)	
		on ethylene passed	on ethylene that reacts	on ethylene passed	on ethylene that reacts
16	20	23,7	68,3	6,6	20,0
17	40	19,6	69,0	5,0	20,8
18	60	19,1	68,4	5,8	21,4
19	80	18,2	68,5	6,3	21,1
20	95	17,5	70,5	5,0	20,9
21	105	16,6	70,5	4,7	21,0

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*Original Russian pagination. See C. B. translation.

BRIEF COMMUNICATIONS

ACTION OF NITROGEN TETROXIDE ON β-NITROSTYRENE

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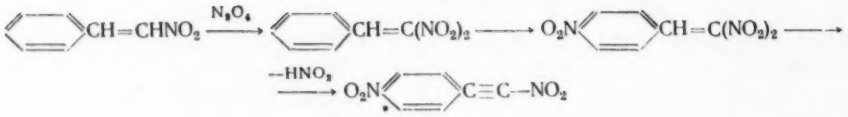
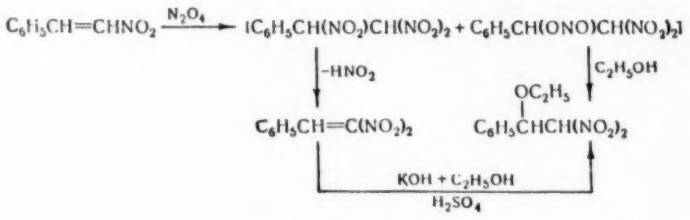
The reaction of N_2O_4 with unsaturated compounds has been studied by many investigators. An examination of literature data shows that the capacity of a double bond to add N_2O_4 is reduced when negative substituents are present and in a number of cases there are side processes associated with oxidation, cyclization, etc. For example, phenylacetylene and diphenylacetylene add one molecule of N_2O_4 with the formation of α, β-dinitrostyrene [1] and dinitrostilbene [2], respectively. A second molecule of N_2O_4 does not add to these compounds. The two nitro groups have a passivating effect on the double bond in this case. It seemed interesting to determine the strength of the effect of one nitro group in such compounds.

For this purpose we studied the reaction of β-nitrostyrene with N_2O_4. When the reaction was carried out in ether, the absorption of N_2O_4 proceeded very slowly and was accompanied by oxidation processes. p-Nitrobenzoic acid was isolated as the sole product of a reaction at 20-25°. If the reaction was carried out at a temperature below 18°, it was possible to isolate in very low yield p-nitrophenylnitroacetylene, the substance obtained previously by Wieland [3] from N_2O_4 and cinnamaldehyde. The reaction apparently proceeded according to the scheme:



If CCl_4 was used as the reaction solvent, then nitration in the benzene nucleus did not occur. The main reaction product in this case was β,β-dinitrostyrene. In addition, 1-phenyl-2,2-dinitroethyl nitrite was apparently formed as the action of alcohol on the reaction mixture formed the ethyl ether of 1-phenyl-2,2-dinitroethanol in addition to β,β-dinitrostyrene. This ether could also be obtained by the action of alcoholic KOH on β,β-dinitrostyrene. The reactions carried out may be represented by the following scheme:



Consequently, the presence of one nitro group at the double bond does not prevent the normal addition of N_2O_4, although it strongly retards it. The reaction products obtained were unstable. It should be noted that β,β-dinitrostyrene is also a very reactive compound; when boiled with water it forms benzaldehyde, which was isolated and characterized. The action of a solution of KOH in aqueous dioxane resulted in a vigorous reaction and the potassium salt of dinitromethane precipitated. Evaporation of the mother liquor gave crystals of a potassium salt, from which a substance with m.p. 111.5-112.5° was obtained in good yield. Judging by the analysis, this product was a mixture of 1-phenyl-2,2-dinitroethanol and β,β-dinitrostyrene.

It is interesting to note that the presence of a second nitro group, even in the benzene nucleus of nitrostyrene, made it completely incapable of adding N_2O_4. After a solution of p,β-dinitrostyrene with N_2O_4 in CCl_4 had stood for 12 days, practically the whole of the dinitrostyrene was recovered unchanged. Only a very small amount of a substance with m.p. 89-90° could be isolated and its structure was not established.

EXPERIMENTAL

p-Nitrophenylnitroacetylene. Into a four-necked flask fitted with a stirrer with a seal, a thermometer immersed in the liquid, a reflux condenser with calcium chloride tube, and a dropping funnel were placed 27.5 g of β-nitrostyrene, 100 ml of absolute ether, and 82 g of pure N_2O_4. The mixture was stirred for 2.5 days at a temperature no higher than 18°. During this time, a further 80 g of N_2O_4 was added as it was absorbed. The precipitate was collected, methanol added to the filtrate, and the latter cooled to -70°. The precipitate obtained was combined with the precipitate obtained directly from the reaction mixture and recrystallized from alcohol. The yield was 0.75 g and the m.p was 139-139.5°. Literature data [3]: m.p. 143°. Found: C 50.24; 50.32; H 2.08; 2.23; N 14.51; 14.49%. $C_8H_4O_4N_2$. Calculated: C 50.01; H 2.10; N 14.58%. The molecular weight found cryoscopically in benzene was 183; calculated 193.13.

β,β-Dinitrostyrene. A solution of 90 g N_2O_4 in 50 ml of dry CCl_4 was added to a solution of 15 g of β-nitrostyrene in 100 ml of dry CCl_4 in a flask with reflux condenser with a calcium chloride tube and the mixture left at room temperature for 5 days. The solvent was removed in vacuum to leave 26 g of yellowish oil. This oil was treated with 10 ml of absolute ethanol and cooled, and β,β-dinitrostyrene collected by filtration. After the product was recrystallized from CCl_4, the yield was 7.5 g (39% of theoretical) and the m.p. 95-96°. Found: C 49.02; 48.98; H 3.27; 3.21; N 14.65; 14.52%. $C_8H_6O_4N_2$. Calculated: C 49.47; H 3.12; N 14.43%.

Ethyl ether of 1-phenyl-2,2-dinitroethanol. In one experiment on the preparation of β,β-dinitrostyrene, the filtrate was evaporated. The residue crystallized on cooling. The crystals obtained were the ethyl ether of 1-phenyl-2,2-dinitroethanol and the yield was 2.5 g (from 5 g of β-nitrostyrene), i.e. 31% of theoretical; the m.p. was 29-31° (from CCl_4).

To a solution of 7.8 g of β,β-dinitrostyrene in ethanol was added excess 20% KOH solution and the potassium salt (6.2 g) collected by filtration; it had decomp. p. 187-188° (from water). Acidification of an aqueous solution of this salt with sulfuric acid yielded 4.7 g of the ethyl ether of 1-phenyl-2,2-dinitroethanol, which sometimes precipitated as crystals with m.p.31-32° (from CCl_4) and sometimes as an oil, which had b.p. 115-117° (3 mm); $n^{20}D$ 1.5048; d_4^{20} 1.2152. Found: C 49.93; 49.91; H 5.01; 5.03; N 11.75; 12.09%. $C_{10}H_{12}O_5N_2$. Calculated: C 50.00; H 5.04; N 11.66%. The equivalent weight was determined by titration with 0.1 N NaOH: Found 240.18; Calculated 240.21.

Potassium salt of the methyl ether of 1-phenyl-2,2-dinitroethanol. This was obtained analogously by the action of KOH in CH_3OH. It was recrystallized from aqueous methanol. The equivalent weight was determined by titration with 0.1 N HCl in the presence of Methyl orange; found 264.2, 262.4; calculated for $C_9H_9O_5N_2K$ 264.3.

Attempt to prepare 1-phenyl-2,2-dinitroethanol. A solution of 0.6 g of KOH in 8 ml of 80% dioxane was gradually added at 0-1° to a solution of 2 g of β,β-dinitrostyrene in 20 ml of 80% dioxane. After 3 hr, the precipitate was collected by filtration and the solution evaporated slightly and again filtered. We obtained 0.4 g of the potassium salt of dinitromethane with decomp. p. 207-208° (from aqueous methanol). Found C 8.33; 8.46; H 0.73; 0.73; N 20.08; 20.17; K 27.47; 27.12%. CHO_4N_2K. Calculated: C 8.33; H 0.70; N 19.43; K 27.13%.

Evaporation of the filtrate from the potassium salt of dinitromethane yielded a decomposing oil, which was treated with 50% CH_3OH to yield 0.08 g of a yellow salt. Acidification of an aqueous suspension of this salt with 50% CH_3COOH yielded 0.07 g of colorless crystals which melted at 111.5-112.5° after recrystallization from isooctane. Found: C 47.26; 47.45; H 3.42; 3.56; N 14.22; 14.56%. This product was apparently a mixture of β,β-dinitrostyrene and 1-phenyl-2,2-dinitroethanol, for which we calculated: C 45.29; H 3.80; N 13.21%, i.e., partial dehydration occurred during the acidification.

SUMMARY

1. The action of N_2O_4 on β-nitrostyrene under various conditions yielded β,β-dinitrostyrene, the ethyl ether of 1-phenyl-2,2-dinitroethanol, and p-nitrophenylnitroacetylene.

2. The addition of alcohols and water to β,β-dinitrostyrene was studied.

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DIENE CONDENSATIONS OF ISOPRENE WITH UNSYMMETRICAL DIENOPHILES

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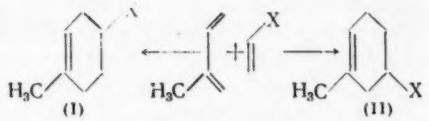
In the condensation of isoprene with unsymmetrical dienophiles, the formation of para and meta adducts (I) and (II) is possible



We previously investigated [1] the ratio of structural isomers in the condensations of isoprene with acrylic acid and its derivatives. To determine the effect of substituents in the dienophile on the structural direction more accurately, in the present work we studied the condensations of isoprene with three other unsymmetrical dienophiles, methyl vinyl ketone, styrene, and nitroethylene. The results obtained, together with results from previous work, are given in the table.

TABLE

Structural Direction in Diene Condensations of Isoprene

Substituent in dienophile	NO_2	C_6H_5	$COCH_3$	CN	CO_2CH_3	CO_2H	CHO
Para : meta ratio	3,7 : 1	3,5 : 1	2,3 : 1	2,2 : 1	2,0 : 1	1,9 : 1	1,8 : 1

As these results show, the nitro group has the greatest directing power, then there is the phenyl group, and the weakest selected direction is shown by various derivatives of acrylic acid, the substituents in which have a similar electronic nature. However, it was not possible to establish any relation between electronic effects of the substituents in all the dienophiles studied and their effect on the structural direction.

EXPERIMENTAL

The diene condensations were carried out by heating a mixture of diene and dienophile in steel ampoules in the presence of 0.1-0.2% hydroquinone.

Condensation of isoprene with methyl vinyl ketone. A mixture of 15 g of isoprene, 9 g of methyl vinyl ketone, and 50 ml of benzene was heated at 200° for 5 hr. We obtained 14.3 g (81%) of a mixture of adducts (I) and (II) (X = $COCH_3$) with b.p. 99–102° (30 mm); n_D^{20} 1.4710 [2]. Dehydrogenation of this mixture of adducts over 15% Pd/C at 350-360° gave 12 g (86%) of a mixture of methylacetophenones, which, without distillation, was oxidized with a solution of 31 g of CrO_3 in acetic acid. The mixture of phthalic acids obtained (10.5g, 71%)

was separated through the barium salts [3] and this yielded 6.8 g of terephthalic and 2.9 g of isophthalic acids (ratio 2.3 : 1).

Condensation of isoprene with styrene. A mixture of 34 g of isoprene and 52 g of styrene was heated at 200° for 10 hr. We obtained 27 g (31%) of a mixture of adducts (I) and (II) (X = C_6H_5) with b.p. 120-122° (10mm); n_D^{20} 1.5356. Found: C 90.60; 90.43; H 9.53; 9.53%. $C_{13}H_{16}$. Calculated: C 90.64; H 9.36%.

A 20 g sample of this mixture of adducts was dehydrogenated over 20% Pd/C at 350-360° and this yielded 16.2 g (83%) of a partially crystalline mixture of dehydrogenation products. Oxidation of 10 g of this mixture in an autoclave at 200° with 100 ml of 10% HNO_3 yielded 9.3 g (79%) of a mixture of phenylbenzoic acids. Crystallization of the latter from acetone and a mixture of hexane with ether gave 6.3 g of p-phenylbenzoic acid with m.p. 221-223° and 1.8 g of m-phenylbenzoic acid with m.p. 161-162°; neither of the acids depressed the melting points of authentic samples. The ratio of para and meta isomers was 3.5 : 1.

Condensation of isoprene with nitroethylene. A mixture of 15 g of isoprene, 10 g of nitroethylene, and 50 ml of benzene was heated at 150° for 10 hr. We obtained 9 g (47%) of a mixture of adducts (I) and (II) (X = NO_2) with b.p. 113-116° (25 mm); n_D^{20} 1.4820. Found: C 32.91; 32.70; H 4.11; 4.12; N 19.20; 19.26%. $C_7H_{11}O_2$. Calculated: C 32.88; H 4.11; N 19.18%.

A 7.5 g sample of the adducts obtained was hydrogenated in 50 ml of alcohol with 0.1 g of Pt/PtO_2. Distillation yielded 7 g (92%) of hydrogenation products with b.p. 105-107° (17 mm). By means of the Nef reaction carried out by the procedure of Wildman et al. [4], from the hydrogenation products we obtained 4.7 g (85%) of a mixture of methylcyclohexanones with b.p. 162-168°. From 2.6 g of this mixture of ketones and 4.5 g of 2,4-dinitrophenylhydrazine we obtained 6.8 g (95%) of a mixture of hydrazones, recrystallization of which from methanol and a mixture of the latter with benzene yielded 4.5 g of the 2,4-dinitrophenylhydrazone of 4-methylcyclohexanone with m.p. 136-137° and 1.2 g of the 2,4-dinitrophenylhydrazone of 3-methylcyclohexanone with m.p. 151-152°. Neither of the isomers depressed the melting points of authentic samples. The ratio of para and meta isomers in the mixture equalled 3.7: 1.

SUMMARY

With respect to orienting power in diene synthesis with isoprene, substituents in dienophiles of the type $CH_2 = CH - X$ may be arranged in the order $NO_2 > C_6H_5 > COCH_3$.

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RELATION BETWEEN THE PRE-EXPONENT AND THE ACTIVATION ENERGY

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In the present work an examination is made of the relation between the activation energy E and the pre-exponent A in the rate constants of the decomposition reaction $XY \rightarrow X^{\cdot} + Y^{\cdot}$ and the radical substitution $X^{\cdot} + RH \rightarrow XH + R^{\cdot}$. Figure 1 shows the change in log A in relation to E for the following decomposition reactions.

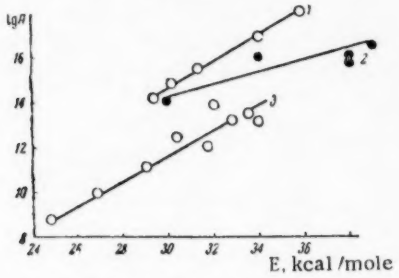

Fig. 1. Relation between log A and E for the decomposition of: 1) aliphatic azo compounds; 2) peroxides; 3) hydroperoxides.

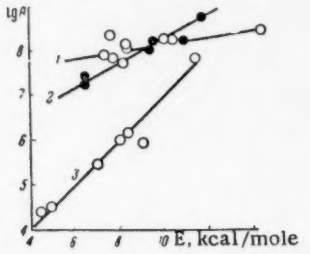

Fig. 2. Relation between log A and E for the radical substitutions: 1) $CH_3^{\cdot} + RH$; 2) $C_3H_7^{\cdot} + RH$; 3) $RO_2^{\cdot} + RH$.

Decomposition of the aliphatic azo compounds $R-N{=}N-R \rightarrow 2R^{\cdot} + N_2$. The radical R· was: $(C_2H_5)(CH_3)(CN)C$; $(CH_3CH_2CH_2CH_2)(CH_3)(CN)C$; $(CH_3)_2(CN)C$; $(COOHCH_2CH_2)(CH_3)(CN)C$; $(CH_3OCO)(CH_3)_2C^{\cdot}$ [1] (they are arranged in order of increasing E). As Fig. 1 shows, for this reaction there is a well-obeyed linear relation between E and log A: $\log A = -3.4 + 0.6\,E$ (A is in sec^{-1} and E in kcal/mole).

Decomposition of peroxides $ROOR' \rightarrow RO^{\cdot} + R'O^{\cdot}$. Figure 1 gives data for benzoyl peroxide, tert-butyl perbenzoate, and isopropylbenzene and tert-butyl peroxides [2]. log A also increases linearly with an increase in E.

For the decomposition of hydroperoxides: $ROOH \rightarrow RO^{\cdot} + {}^{\cdot}OH$ [3, 4], the following linear relation between log A and E is also obeyed quite well: $\log A = -5.2 + 0.56\,E$. The symbatic nature of the changes in A and E for monomolecular decompositions was examined in [5].

A linear relation between log A and E ($\Delta \log A = \beta \Delta E$, E in kcal/mole) is also found for radical substitution, as is shown by Fig. 2, which gives data for the reactions: $CH_3^{\cdot} + RH \rightarrow CH_4 + R^{\cdot}$ (RH is a hydrocarbon, gas phase [6], $\beta = 0.08$), $C_3H_7^{\cdot} + RH \rightarrow C_3H_8 + R^{\cdot}$ (RH is a hydrocarbon or aldehyde, C_3H_7 is a primary or secondary propyl radical, gas phase [7], $\beta = 0.27$), and $RO_2^{\cdot} + RH \rightarrow ROOH + R^{\cdot}$ (RH is a hydrocarbon in which a methylene group is attacked, liquid phase, $\beta = 0.5$) [4, 8].

As an example of ionic reactions, we can cite the reaction: $ROOH + Fe^{+2} \rightarrow RO^{\cdot} + Fe^{+3} + OH^-$, for which the following relation is fulfilled: $\Delta \log A = 0.26\,\Delta E$ (ROOH is hydrogen peroxide or peroxides of cumene and its

homologs [2]. The examples presented show that proportionality between log A and E is found in a wide range of different chemical reactions and its study deserves serious attention.

TABLE

Hydrocarbon	E in kcal/mole	A found	A calculated, liter/mole,sec
Tetralin	4.5	$2.7 \cdot 10^4$	$2 \cdot 10^4$
Ethyl linoleate	5	$3.0 \cdot 10^4$	$3 \cdot 10^4$
1-Octene	7	$3.6 \cdot 10^5$	$3 \cdot 10^5$
1-Methylcyclohexene	8	$1.1 \cdot 10^6$	$1 \cdot 10^6$
Cyclohexene	8.5	$1.5 \cdot 10^6$	$2 \cdot 10^6$
Dihydromyrcene	9	$1.0 \cdot 10^6$	$3 \cdot 10^6$
Ethylbenzene	11.4	$7.2 \cdot 10^7$	$5 \cdot 10^7$
1,3,5-Trimethylcyclohexene	7		$3 \cdot 10^5$
1,2-Dimethylcyclohexene	7.5		$6 \cdot 10^5$
4-Methyl-3-heptene	8.1		$1 \cdot 10^6$
Cyclohexane	12		$1 \cdot 10^8$
n Decane	13		$3 \cdot 10^8$

The relation between A and E may be used for finding absolute values of k from values of E. The determination of k for radical reactions requires a complex experiment, while activation energies may be determined in comparatively simple experiments. If the relation of A and E is known, it is comparatively easy to determine A and hence k from the value of E. As an example, let us examine the reaction $RO_2^{\cdot} + RH$, for which the following reaction is obeyed well: $\log A = 2.0 + \frac{1}{2} E$. The values of A calculated by this formula are compared with experimental data in the table and the small discrepancy between them indicates that the values of A found solely by calculation are close to the true values.

The relation between A and E has direct bearing on the problem of the relation between the reactivity of molecules and radicals and their structure. The relative activity of two molecules (we will denote them by the indices 1 and i) in the same type of reaction is expressed qualitatively through the ratio of the constants k_i/k_1 or $\log k_i/k_1$. If the following equation is fulfilled:

$$\log A_i = B + \beta E_i \tag{1}$$

then

$$\log k_i/k_1 = [\beta - (1000/4.6\,T)]\,\Delta E. \tag{2}$$

At constant temperature, $\beta - (1000/4.6 \cdot T) = \text{const}$ and the relative activity is determined solely by the difference in the activation energies ΔE. As Semenov [9] showed, for different reactions there is a linear relation between E and the heat of reaction q:

$$E = A - \alpha \cdot q \tag{3}$$

The empirical relations (1) and (3) make it possible to relate unequivocally a kinetic value, namely, the reaction rate constant, to a thermodynamic value, the heat of reaction:

$$\log k = B + [\beta - (1000/4.6\,T)](A - \alpha q). \tag{4}$$

Relation (4) is of practical value in that it makes it possible to determine k from the value of q, and of fundamental value in that it shows the existence of an unequivocal relation between the thermodynamics and kinetics of elementary reactions.

Relation (2) makes it possible to draw an interesting conclusion on the temperature "inversion" of relative reactivity for a group of substances in a given reaction. Let us assume that the substance with index i is more active than that with index 1: $k_i > k_1$ or $\log k_i/k_1 > 0$. Normally, $k_i > k_1$ if $E_i < E_1$, i.e., $\Delta E = E_i - E_1 < 0$. At sufficiently low values of T, $(1000/4.6T) > \beta$ and $\log k_i/k_1 = [\beta - (1000/4.6 \cdot T)]\Delta E > 0$. With an increase in T, there arrives a moment (at $T = T_i$) when there is the equality: $\beta = 1000/4.6 \cdot T_i$ (5) and $k_i = k_1$. When $T > T_i$, k_1 becomes less than k_1, i.e., substance i becomes less active than substance 1, and there is inversion of the relative activity of substances i and 1 (T_i is the relative activity inversion temperature). Due to the approximate nature of relation (2), for a group of substances one would expect a temperature region $T_i \pm \Delta T$, in which all the values of k_i are approximately the same. By using formula (5) for the decomposition of aliphatic azo compounds we obtain $T_i \approx \approx 90°$, for the decomposition of hydroperoxides $T_i \approx 125°$, and for the reaction $RO_2^{\cdot} + R_1R_2CH_2$ $T_i \approx 160°$. If β is small, then the relative activity inversion temperature is practically inaccessible. The conclusion on temperature inversion necessitates a reexamination of contemporary ideas on the relative activity of substances in

chemical reactions. The ratio of the activation energies itself does not give an indication of which substance is more active and by how much. The activity of different molecules may be assessed only when, in addition to E, the temperature and coefficient β in relation (2) for reactions of the given type are known. Temperature inversion of the relative activity is important in controlling the composition of products in multicomponent chemical processes, for example, in hydrocarbon oxidations.

SUMMARY

1. For decomposition and radical substitution reactions there is a linear relation between the logarithm of of the pre-exponent and the activation energy.

2. This relation was used for calculating the elementary rate constants of reactions of the type $RO_2^{\cdot} + RH$.

3. A conclusion was drawn on the temperature inversion of the relative activity of substances for which this relation is fulfilled.

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SYNTHESIS OF PRIMARY γ-ORGANOSILICON ACETYLENE ALCOHOLS

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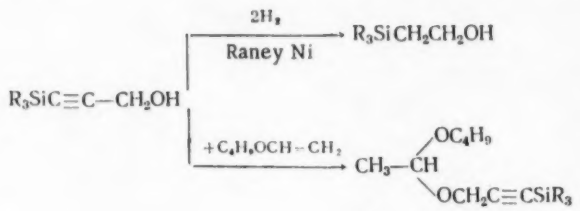
In previous papers [1-4], we described methods of preparing mono-, di-, and trihydric γ-silicon- and germanium-containing secondary and tertiary acetylene alcohols. Continuing the investigation in this direction, in the present work we developed a method for preparing primary γ-silicon-containing alcohols. The basis of the synthesis of primary γ-silicon-containing alcohols was the reaction of the dibromodimagnesium derivative of propargyl alcohol with an alkyl(aryl)chlorosilane:

$$R_3SiCl + BrMgC{\equiv}C{-}CH_2OMgBr \longrightarrow R_3SiC{\equiv}C{-}CH_2OH$$

(where R is alkyl or aryl). The structure of the alcohols obtained was demonstrated by hydrogenation and acetal formation according to the scheme:



γ-Hydroxypropyltrimethylsilane has been described in the literature [5]. The constants of the alcohol we obtained by hydrogenation of 3-trimethylsilylpropyn-2-ol-1 agreed completely with literature data.

EXPERIMENTAL

Synthesis of 3-trimethylsilylpropyn-2-ol-1 $(CH_3)_3SiC{\equiv}C{-}CH_2OH$. Into a 2-liter, three-necked, round-bottomed flask fitted with a mechanical stirrer, dropping funnel, reflux condenser, and thermometer, were placed 48.6 g (2 g-atom) of magnesium turnings and 500 ml of dry ether. Then 218 g (2 moles) of ethyl bromide was added dropwise with stirring and cooling. To the Grignard reagent formed was added 56 g (1 mole) of propargyl alcohol dropwise with stirring and cooling. Gas was evolved and a white, curdy precipitate formed. The reaction mixture was stirred for 2 hr with cooling and for 3 hr with heating on a water bath. Then 2 g of cuprous chloride was introduced into the flask and 108.5 g (1 mole) of trimethylchlorosilane added gradually with cooling and stirring. The mixture formed was stirred for 2 hr at room temperature and for 8 hr with heating on a water bath. At the end of the synthesis, the reaction mixture was cooled and stirred and treated with 150 ml of moist ether and then 5% aqueous hydrochloric acid until the precipitate dissolved completely. The ether

TABLE

Physicochemical Constants of Organosilicon Compounds Obtained

Formula	B. p. in °C (p in mm Hg)	n_D^{20}	d_4^{20}	MR found	MR calculated	Si in % found	Si in % calculated	Yield in %
$(CH_3)_3SiC\equiv C\cdot CH_2OH$	61 (2)	1,4523	0,8806	39,31	39,48	21,39 21,52	21,9	40,2
$(C_2H_5)_3SiC\equiv C\cdot CH_2OH$	109—110 (6)	1,4670	0,8932	52,92	53,37	16,12 16,30	16,49	44,7
$(CH_3)_2C_6H_5SiC\equiv C\cdot CH_2OH$	131—132 (2)	1,5335	0,9996	59,43	59,15	14,51 14,62	14,76	67,8
$CH_3-CH(OC_4H_9)-OCH_2C\equiv CSi(CH_3)_3$	95 (5)	1,4378	0,8683	69,02	69,25	11,95 11,87	12,29	71,0
$(CH_3)_3SiCH_2CH_2CH_2OH$*	61—62 (10)	1,4295	0,8406	40,61	41,09	—	—	90,0

* Described in the literature.

layer was separated from the aqueous layer and the latter was extracted with ether. The ether layer and ether extracts were combined, washed with distilled water until neutral, and dried over calcium chloride. The ether was removed and the residue vacuum distilled.

Fractions were obtained: Fraction I had b.p. 30-61° (2 mm); n_D^{20} 1.4465; 6 g, Frac. II ; b.p. 61-62° (2 mm); n_D^{20} 1.4523; 54.8 g.

Redistillation of the last fraction yielded 51.5 g (40.2%) of substance with b.p. 61° (2 mm); n_D^{20} 1.4523; d_4^{20} 0.8806. Found: MR 39.31. $C_6H_{12}SiO$. Calculated: MR 39.48. Found: Si 21.39; 21.52%. Calculated: Si 21.9%.

3-Triethylsilylpropyn-2-ol-1 and 3-dimethylphenylsilylpropyn-2-ol-1 were synthesized analogously and their physicochemical constants are given in the table.

Synthesis of 3-trimethylsilylpropyn-2-yl butyl acetal $CH_3-CH(OC_4H_9)-OCH_2C\equiv CSi(CH_3)_3$. Into a 25-ml, three-necked, round-bottomed flask, fitted with a mechanical stirrer, reflux condenser, and thermometer were placed 5 g (0.05 mole) of vinyl butyl ether and 6.4 g (0.05 mole) of 3-trimethylsilylpropyn-2-ol-1. Then 1 drop of concentrated hydrochloric acid was added with stirring. The mixture was heated up to 79°. For completion of the reaction the mixture was heated for a further 2 hr at 100° and left overnight. The reaction mixture was then neutralized with baked potassium carbonate, filtered, and vacuum distilled. Fractions were obtained: Fraction I had b.p. 75-94° (5 mm); n_D^{20} 1.4308; 1.9 g; Fraction II had b.p. 94-95° (5 mm); n_D^{20} 1.4378; 8.8 g.

Redistillation of fraction II yielded 8.1 g (71%) of a substance with b.p. 95° (5 mm); n_D^{20} 1.4378; d_4^{20} 0.8683. Found MR 69.02. $C_{12}H_{24}SiO_2$. Calculated MR 69.25. Found: Si 11.95; 11.87%. $C_{12}H_{24}SiO_2$. Calculated: Si 12.29%.

Synthesis of 3-trimethylsilylpropanol-1 $(CH_3)_3SiCH_2CH_2CH_2OH$. The hydrogenation was carried out in an autoclave in ethanol over Raney nickel. For the hydrogenation we used 12.8 g (0.1 mole) of 3-trimethylsilylpropyn-2-ol and ~1 g of Raney Ni in 50 ml of ethanol. The usual treatment yielded 11.6 g (90%) of a substance with b.p. 61-62° (10 mm); n_D^{20} 1.4295; d_4^{20} 0.8406. Literature data [5]: b.p. 62-63° (10 mm); n_D^{20} 1.4238; d_4^{20} 0.8408.

SUMMARY

1. The reaction of trialkyl(aryl)chlorosilanes with the dimagnesium derivative of propargyl alcohol was studied. A method was developed for preparing primary γ-silicon-containing acetylene alcohols.

2. 3-Trimethylsilylpropyn-2-ol-1, 3-dimethylphenylsilylpropyn-2-ol-1, 3-triethylsilylpropyn-2-ol-1, and 3-trimethylsilylpropyn-2-yl butyl acetal were obtained for the first time.

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BEHAVIOR OF AMINOTETRAZOLES IN THE MANNICH REACTION

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To study the behavior of various heterocyclic amines in the Mannich reaction, we prepared some previously known amines of the tetrazole series. We were interested in determining the possibility of condensing these amines with formaldehyde and nitroform or directly with β,β,β-trinitroethanol and establishing the conditions of this reaction accurately.

For the condensation we used: 5-aminotetrazole [1], 1-methyl- and 2-methyl-5-aminotetrazoles [2], and also 1-ethyl- and 2-ethyl-5-aminotetrazoles [2], which we prepared according to the procedures described in the literature. As a result of the work it was established that 5-aminotetrazole does not undergo the condensation reaction, while 1- and 2-alkyl-5-aminotetrazoles readily undergo this reaction and give 1- and 2-alkyl-5-trinitroethylaminotetrazoles in approximately equally good yields. This difference in the behavior of 5-aminotetrazole, on the one hand, and 1- and 2-alkyl-5-aminotetrazoles, on the other, evidently must be explained by the appearance of basic properties of the amino groups of 5-aminotetrazoles when alkyl radicals replace the hydrogen atom of the NH group of the ring, which has the properties of an acid hydrogen, forming salts with bases.

EXPERIMENTAL

1-Methyl-5-trinitroethylaminotetrazole. With stirring and cooling, 5.4 ml of 30% of an aqueous solution of formaldehyde was added to 9 g of nitroform (0.06 mole) with the temperature of the mixture no higher than 35°, and then the mixture was kept at 20° for 1 hr. It was then diluted with 25 ml of water and 4 g of 1-methyl-5-aminotetrazole (0.04 mole) added. The reaction mixture was heated with stirring to 50-55° and kept at this temperature for 1 hr; thereupon the undissolved 1-methyl-5-aminotetrazole dissolved completely and the solution became clear, but after a few minutes it became turbid. The mixture was cooled to room temperature and the slightly yellowish product was collected by filtration, washed with cold water to remove excess nitroform and formaldehyde until the filtrate became colorless, and dried in air. The yield of 1-methyl-5-trinitroethylaminotetrazole was 7.52 g (70.9%); it had m.p. 137-138° (from dichloroethane). Found: C 18.39; 18.24; H 2.40; 2.29; N 43.65; 43.74%. $C_4H_6N_8O_6$. Calculated: C 18.34; H 2.31; N 42.77%.

1-Methyl-5-trinitroethylaminotetrazole dissolves readily in alcohol and acetone. It is insoluble in cold water and ether. When heated with nitric acid (sp. g. 1.35) until solution was complete (~70-80°) it formed the nitrate of 1-methyl-5-trinitroethylaminotetrazole as white, lustrous crystals with m.p. 104-105°. The salt was unstable toward water. When the salt was washed with water to a neutral reaction to litmus, the nitric acid was washed out and 1-methyl-5-trinitroethylaminotetrazole with m.p. 137° remained.

2-Methyl-5-trinitroethylaminotetrazole. With stirring and cooling, 2.3 ml of a 30% aqueous solution of formaldehyde was added to 3.81 g of nitroform (0.025 mole) with the temperature of the mixture kept at 20-35° and then the mixture was kept at 20° for 30 min. The mixture was then diluted with 25 ml of water and 2 g of

2-methyl-5-aminotetrazole (0.02 mole) added at room temperature. After a few minutes a precipitate began to form. The reaction mixture was heated to 30-35°, kept at this temperature for 1 hr and then cooled to 0-2° for 1 hr. The precipitate formed was collected, washed with water to remove excess nitroform and formaldehyde and dried in air. The yield of 2-methyl-5-trinitroethylaminotetrazole was 4.65 g (~90%) and the m.p. was 125° (from $CHCl_3$ or by precipitation from nitric acid with water). Found C 18.45; 18.51; H 2.30; 2.07; N 43.39; 43.19%. $C_4H_6N_8O_6$. Calculated: C 18.34; H 2.31; N 42.77%.

To a solution of 4.58 g of trinitroethanol (0.025 mole) in 25 ml of water at 35-40° was added 2 g of 2-methyl-5-aminotetrazole (0.02 mole). The reaction mixture was heated to 50° and cooled slowly to room temperature and then to 5°. The precipitate was collected, washed with water and dried in air. The yield of 2-methyl-5-trinitroethylaminotetrazole was 5.28 g (100%) and the m.p. 125°. 2-Methyl-5-trinitroethylaminotetrazole is insoluble in cold water, but dissolves in acetone.

1-Ethyl-5-trinitroethylaminotetrazole. With stirring and cooling with iced water, 2 ml of a 30% aqueous solution of formaldehyde was added to 3.2 g of nitroform (0.021 mole) with the mixture kept at 20-35° and then the mixture was kept at 20° for 1 hr. It was diluted with 25 ml of water and 2 g of 1-ethyl-5-aminotetrazole (0.0177 mole) added at 20°. The mixture was heated to 60° and kept at this temperature for 1 hr. After the mixture had been cooled to 10°, the crystalline product was collected, washed with water, and dried in air. We obtained 2.47 g(50.6% yield) of 1-ethyl-5-trinitroethylaminotetrazole with m.p. 134-135° (from dichloroethane). Found: C 21.88; 22.00; H 3.34; 3.23; N 40.87; 41.04%. $C_5H_8N_8O_6$. Calculated: C 21.76; H 2.92; N 40.60%. 1-Ethyl-5-trinitroethylaminotetrazole is difficultly soluble in cold water, alcohol, and dichloroethane, and dissolves readily in acetone.

2-Ethyl-5-trinitroethylaminotetrazole. To 3.4 g of nitroform at 20-35° was added 2.1 ml of a 30% aqueous solution of formaldehyde and the mixture kept for 1 hr. It was then diluted with 25 ml of water and 2 g of 2-ethyl-5-aminotetrazole added at 30°. The mixture was heated for 1 hr at 35-40°. After it had been cooled to 10°, the oil formed was washed with cold water to remove excess nitroform and formaldehyde, when it crystallized. The crystals were dissolved in 50 ml of nitric acid and the solution poured into a 10-fold amount of cold water. The white precipitate was collected, washed well with water, and dried in air. We obtained 2.5 g of 2-ethyl-5-trinitroethylaminotetrazole (51.23% yield) with m.p. 99-100° (from CCl_4).

A solution of 4 g of trinitroethanol in 25 ml of water was mixed with 2 g 2-ethyl-5-aminotetrazole (25% excess of trinitroethanol). The mixture was heated at 35-40° for 1 hr and cooled to 10°. The precipitated oil was washed with cold water to remove excess trinitroethanol, when it crystallized. The crystals were dissolved in 50 ml of nitric acid (sp. g. 1.35) and the solution poured into a 10-fold amount of water. The precipitate was collected, washed carefully with water, and dried in air. We obtained 2.07 g of 2-ethyl-5-trinitroethylaminotetrazole (42.4% yield) with m.p. 99-100° (from CCl_4). 2-Ethyl-5-trinitroethylaminotetrazole dissolves readily in acetone, is difficultly soluble in cold, but readily soluble in hot CCl_4, and is insoluble in water and dichloroethane. Found: C 21.80; 21.92; H 3.34; 3.23; N 40.58; 40.72%. $C_5H_8N_8O_6$. Calculated: C 21.76; H 2.92; N 40.60%.

SUMMARY

1. The behavior of 5-aminotetrazole and 1- and 2-alkyl-5-aminotetrazoles in the Mannich reaction with formaldehyde and nitroform was investigated.

2. 5-Aminotetrazole does not undergo the Mannich reaction, but 1- and 2-alkyl-5-aminotetrazoles readily give 1- and 2-alkyl-5-trinitroethylaminotetrazoles.

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ACTION OF BROMINE AND TERT-BUTYL CHLORIDE ON METHYL-2-FURYL KETONE IN THE PRESENCE OF EXCESS ALUMINUM CHLORIDE

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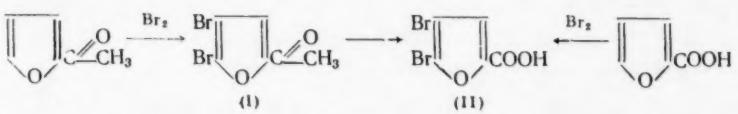
One of us and Vol'kenshtein [1] showed that the Pearsoh–Pope method [2] of blocking the side chain of aromatic ketones with aluminum chloride makes it possible to change the bromination of 2-acetothienone in such a way that there is substitution in the ring with the formation of mainly 4-bromo-2-acetothienone. It seemed interesting to determine how methyl-2-furyl ketone (MFK) would react under similar conditions,as this compound is brominated in the side chain without catalyst [3] or in the presence of a very small amount. It is known [4-7] that in the halogenation of furan derivatives with an electronegative substituent in position 2, the predominant role is played by the α-orienting effect of the ring oxygen, which is apparently stronger than the effect of the heteroatom in thiophene. For example, the bromination of furfural yields only 5-bromofurfural [4], while 2-thiophenealdehyde forms a mixture of the 4- and 5-isomers [8], though with a predominance of the latter. Nonetheless, according to Pearson (see above) the direction of the reaction in the bromination of MFK was more difficult to determine.

It was also advantageous to determine how MFK would react with an alkyl halide under conditions when this ketone is present in the form of a complex with aluminum chloride. In this connection, it should be pointed out that the Friedel-Crafts alkylation of furfural with isopropyl chloride forms 4-isopropylfurfural [9] while tert-butyl enters position 5 of the nucleus to form 5-tert-butylfurfural [10].

The results we obtained may be summarized as follows: In the action of bromine on MFK at room temperature in the presence of 3 moles of aluminum chloride without solvent, the furan ring is attacked, but, in contrast to the case of 2-acetothienone, the reaction with MFK could not be stopped at the formation of a monobromo derivative. It was only with a low temperature and a short experiment that it was possible to isolate a small amount of the monobromo derivative, methyl-5-bromo-2-furyl ketone, together with methyl 4,4-dibromo-2-furyl ketone (I), which forms the bulk of the product from the reaction of bromine with MFK at room temperature. The yield of the latter was increased from 34 to 62% if the molar ratio of bromine and MFK was 2:1.

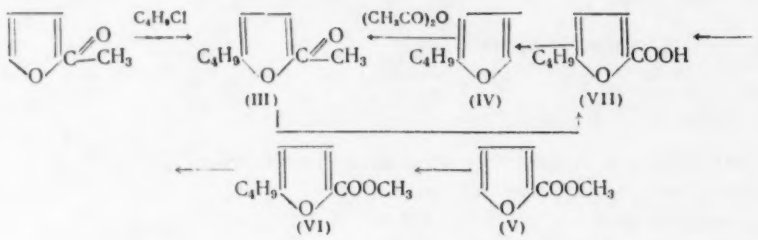
The structure of (I) was demonstrated by oxidation to known 4,5-dibromo-2-furancarboxylic acid (II), which was identical with (II) obtained by direct bromination of 2-furancarboxylic acid [7]:



(I) (II)

Of the three methods of oxidizing (I), namely, with $K_3Fe(CN)_6$ [11], $KMnO_4$ [3] or NaOCl [12], the last method was found to be the best; the acid yield was then 84%.

By the action of tert-butyl chloride on MFK in the presence of excess aluminum chloride we obtained methyl tert-butyl-2-furyl ketone (III). It was found to be identical in the melting points of the semicarbazone and 2,4-dinitrophenylhydrazone with the product we obtained by acetylation of tert-butylfuran (IV), which in its turn was synthesized by Gilman's method [13] by tert-butylation of methyl 2-furancarboxylic acid (V), hydrolysis of (VI), and decarboxylation of the 5-tert-butyl-2-furancarboxylic acid (VII) formed. If, as Gilman considered, we assume that this route leads to (IV), then our ketone, which was formed by the action of tert-butyl chloride on MFK, should be assigned structure (III). On oxidation with NaOCl [12] this ketone gives (VII), described by the investigator mentioned.



EXPERIMENTAL

Bromination of MFK. Over a period of 1.5 hr, 24.7 g of MFK was added to 89.7 g of $AlCl_3$ at 0-10° and then 27.7 ml of dry bromine was added to the complex dropwise at 20-25° over a period of 2 hr and the mixture left at 24-25° for 14 hr and then poured onto a mixture of ice and 10 ml of HCl. The oil liberated was extracted with ether and the extract washed with sodium carbonate and hyposulfite solutions and water, dried over $MgSO_4$, and vacuum distilled. Two distillations yielded 37.3 g of (I) (yield 62%) with b.p. 98-110° (4 mm) and m.p. 54.5-55.5° from ligroin. Found: C 27.06; 26.96; H 1.73; 1.67; Br 58.75; 59.01%. $C_6H_4Br_2O_2$. Calculated: C 26.90; H 1.51; Br 59.66%. The oxime had m.p. 148-149° (with decomposition, from alcohol). Found: N 5.54; 5.30%. $C_6H_5Br_2NO_2$. Calculated: N 5.21%. We also isolated two bromides in amounts of 1.5 g and 0.75 g and the first of these was not investigated further, while the second, which had m.p. 92-92.3° (from alcohol) was found to have the elementary composition: $C_6H_3Br_3O_2$.

4,5-Dibromo-2-furancarboxylic acid (II). Oxidation [12] of 10.5 g of (I) yielded 8.9 g of (II) with m.p. 168-168.5° (from water); the yield was 84.2%. Literature data [14]: m.p. 168-168.5°. Found: C 22.21; 22.54; H 0.64; 0.74; Br 59.14; 59.33%. $C_5H_2Br_2O_3$. Calculated: C 22.25; H 0.75; Br 59.22%.

Bromination of MFK at low temperature. To 74.5 g of $AlCl_3$ at 0-5° was added 20.5 g of MFK over a period of an hour and then 10.5 ml of bromine over a period of 1.5 hr at -5 to -6°. After being stirred for 40 min at 21°, the mixture was treated as in the first experiment. Two vacuum distillations yielded 1.45 g (4% yield) of methyl 5-bromo-2-furyl ketone with b.p. 73-75° (4 mm) and m.p. 94-95° (from ligroin). Found: C 38.26; 38.42; H 2.70; 2.77%. $C_6H_5BrO_2$. Calculated: C 28.12; H 2.67%. The oxime had m.p. 78-79° (from aqueous alcohol). Literature data [15]: the ketone has m.p. 94-95° and the oxime m.p. 79.5°. We also obtained 7.2 g (14% yield) of (I) with b.p. 98-110° (4 mm) and m.p. 54-55°.

Methyl 5-tert-butyl-2-furyl ketone (III). To 19.6 g of $AlCl_3$ at 5° was added 5.4 g of MFK over a period of 40 min and then 4.5 g of t-C_4H_9Cl dropwise at 10-15°; the mixture was left at 25° for 21 hr, heated at 30-40° for 2 hr, and treated as described above. Two distillations yielded 3.9 g (48% yield) of (III) with b.p. 78.5° (4 mm) and b.p. 125-126° (10 mm); n_D^{20} 1.4920; Found: C 71.71; 71.85; H 8.55; 8.47%. $C_{10}H_{14}O_2$. Calculated: C 72.26; H 8.49%. The semicarbazone had m.p. 200-201° (with decomposition, from alcohol, in a sealed tube). Found: N 18.43; 18.67%. $C_{11}H_{17}N_3O_2$. Calculated: N 18.82%. The 2,4-dinitrophenylhydrazone had m.p. 219° (from ethylacetate–alcohol). Found: N 15.96; 16.15%. $C_{16}H_{20}N_4O_5$. Calculated: N 16.08%. In addition, we obtained 0.3 g of a substance which was not investigated.

5-Tert-butyl-2-furancarboxylic acid (VII). Oxidation [12] of 1.2 g of (III) yielded 0.7 g (54% yield) of (VII) with m.p. 104-105° (from aqueous alcohol). It did not depress the melting point of (VII) obtained by hydrolysis of (VI). Literature data [13]: m.p. 104-105°.

Acetylation of 5-tert-butylfuran. From 4.8 g of (IV) and 8.2 g of acetic anhydride in the presence of 3.2 g of $ZnCl_2$ [16] we obtained 3.9 g (~61% yield) of (III) with b.p. 125-126° (10 mm); n_D^{20} 1.4921. The semicarbazone (m.p. 200-201°) and 2,4-dinitrophenylhydrazone (m.p. 219-220°) did not depress the melting points of the samples described above.

SUMMARY

Methyl 2-furyl ketone is brominated in the nucleus in the presence of 3 moles of aluminum chloride without solvent.

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"BINDING" OF WATER BY IONS

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On the example of activity coefficients, it was previously shown [1] that allowance for the "binding" of water by ions is insufficient to explain the deviations of the Debye–Hückel theory [2] from experiment. In the present communication we examine the case of heats of dilution.

From Glueckauf's equation for the activity coefficient [3] it is possible to obtain an expression for the relative partial molal heat content $\bar{L}_2$ of an electrolyte, which has the form:

$$\bar{L}_2 = (\bar{L}_2)_D - RT^2\left\{\left[0{,}018m\frac{(r+h-\nu)(2+0{,}018mr)}{(1+0{,}018mr)^2} - \frac{3\nu S_V\sqrt{c}}{2V_w^0(r+h)^2}\right]\frac{\partial r}{\partial T} + \right.$$
$$+\left[\frac{0{,}018m(r+h)}{(1+0{,}018mr)(1-0{,}018mh)} + \ln\frac{1+0{,}018mr}{1-0{,}018mh} - \frac{3\nu S_V\sqrt{c}}{2V_w^0(r+h)^2}\right]\frac{\partial h}{\partial T} - \quad (1)$$
$$\left. - \frac{3(r+h-\nu)(S_E-\alpha_0 S_V)\sqrt{c}}{2V_w^0(r+h)}\right\},$$

where $(\bar{L}_2)_D$ is the corresponding value from theory [2], m is the molality, $r = \varphi_V/V_w^0$, φ_V is the apparent molar volume of the electrolyte, V_w^0 is the molar volume of water, h is the effective number of "bound" water molecules determined according to [1], ν is the number of ions formed by the dissociation of one electrolyte molecule, S_V is the coefficient in the equation $\varphi_V = \varphi_V^0 + S_V\sqrt{c}$ [4]; and c is the volume concentration. In the derivation of equation (1), the thermal expansion coefficients of the solution and pure water were taken to be approximately equal; $\alpha \approx \alpha_0$. For $\partial h/\partial T$ we have:

$$\frac{\partial h}{\partial T} = \sum_i\left\{\frac{b_i\exp(\Delta E_i/RT)-1}{b_i\exp(\Delta E_i/RT)+1}\cdot\frac{\partial n_i}{\partial T} - \frac{2n_i b_i\exp(\Delta E_i/RT)}{RT^2}\cdot\right.$$
$$\left.\cdot\frac{\Delta E_i + T(\partial\Delta E_i/\partial T)}{[b_i\exp(\Delta E_i/RT)+1]^2}\right\}, \quad (2)$$

where $b_i = \tau_i^0/\tau^0$. The value of $\partial n_i/\partial T$ may be determined from the approximate equation [5]

$$\frac{\partial n_i}{\partial T} = n_i\left(\frac{1}{n}\frac{\partial n}{\partial T} - \frac{\Delta E_i}{RT^2}\right). \quad (3)$$

Determination of $\partial h/\partial T$ from experimental data by equation (1) leads to the values $-1.25\cdot10^{-2}$ and

$-1.36 \cdot 10^{-3}$ for NaCl and KCl at 25°. The approximate calculation, assuming that $\partial \Delta E_i / \partial T \approx 0$, gives the corresponding values of $-2.2 \cdot 10^{-3}$ and $5.0 \cdot 10^{-4}$. The discrepancy between the experimental and calculated values of $\partial h / \partial T$ is substantially greater than that between the analogous values of h found previously [1]. This was to be expected, considering that the calculation of heats of dilution is more sensitive to the inadequacy of the theory than the calculation of activity coefficients [4]. Thus, the inadequacy of introducing only one correction for the "binding" of water by ions becomes obvious.

In principle, equations (1) and (2) make it possible to determine the values of $\partial \Delta E_i / \partial T$ from experimental data on heats of dilution. Thereupon, equation (3) should be written in the more general form:

$$\frac{\partial n_i}{\partial \Gamma} = n_i \left(\frac{1}{n} \cdot \frac{\partial n}{\partial T} - \frac{\Delta E_i}{R T^2} + \frac{1}{RT} \cdot \frac{\partial \Delta E_i}{\partial T} \right),$$

which extends its field of application somewhat. A knowledge of the values of $\partial \Delta E_i / \partial T$ would make it possible to find the values of $\partial n_i / \partial T$ more accurately and hence approach a conclusive solution of the problem of the change in mean ionic diameters with temperature.

SUMMARY

We confirmed the inadequacy of the correction for "binding" of water by ions for explaining the discrepancy between the electrostatic theory in [2] and experiment.

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REACTION OF TETRA-n-BUTYLMERCAPTODIBORANE WITH UNSATURATED COMPOUNDS

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As we established previously, in contrast to di-n-butylmercaptodiborane, tetra-n-butylmercaptodiborane does not react with olefins at room temperature in ether [1]. On further investigation it was found that olefins (1-hexene, 1-octene, and styrene) react with tetra-n-butylmercaptodiborane at 70-80° in the presence of pyridine with the formation of n-butyl esters of alkylthioboric acids according to the equation

$$[(C_4H_9S)_2BH]_2 + 2CH_2{=}CHR \longrightarrow 2(C_4H_9S)_2BCH_2CH_2R$$
$$R = n\text{-}C_4H_9,\quad n\text{-}C_6H_{13};\quad C_6H_5.$$

Cyclohexene and methyldiethylvinylsilane react with tetra-n-butylmercaptodiborane under analogous conditions to form n-butyl esters of cyclohexylthioboric and 2-methyldiethylsilylethylthioboric acids (I), respectively.

$$(C_2H_5)_2CH_3SiCH_2CH_2B\,(SC_4H_9)_2 \qquad (I)$$

The reactions between tetra-n-butylmercaptodiborane and propene or isobutene are complex. Heating a mixture of tetra-n-butylmercaptodiborane and propene in the presence of pyridine in an autoclave at 70-80° and 5-15 atm formed the n-butyl ester of n-propylthioboric acid and also the n-butyl ester of di-n-propylthioboric acid and tri-n-butyl thioborate. Tetra-n-butylmercaptodiborane reacted analogously with isobutene, giving a mixture of esters of isobutylthioboric and diisobutylthioboric acids and tri-n-butyl thioborate. The formation of esters of dialkylthioboric acids and the thioborate is explained by the fact that in these cases the tetra-n-butylmercaptodiborane was symmetrized to thioborate and di-n-butylmercaptodiborane. The latter reacted with olefins, giving the corresponding esters of dialkylthioboric acids.

$$(C_4H_9SBH_2)_2 + CH_2{=}CH{-}R \longrightarrow 2C_4H_9SB\,(CH_2CH_2R)_2$$

EXPERIMENTAL

All operations with organoboron compounds were carried out in a nitrogen atmosphere.

n-Butyl n-hexylthioborate. A mixture of 7 g (0.018 mole) of tetra-n-butylmercaptodiborane, 7 g (0.083 mole) of 1-hexene, and 0.5 ml of pyridine was placed in a two-necked flask with a nitrogen inlet and a reflux condenser and heated at 70° for 3 hr. The excess hexene was removed in a water-pump vacuum and then the residue distilled. We obtained 9.0 g (89%) of n-butyl n-hexylthioborate with b.p. 97-98° (0.06 mm); d_4^{20} 0.8860; n_D^{20} 1.4840. Found: C 61.47; 61.43; H 11.26, 11.36%. $C_{14}H_{31}BS_2$. Calculated: C 61.29; H 11.39%.

n-Butyl n-octylthioborate. A mixture of 7 g (0.0185 mole) of tetra-n-butylmercaptodiborane, 8.3 g (0.074 mole) of 1-octene, and 0.5 ml of pyridine was heated for 3 hr at 70°. After removal of the excess octene in

vacuum, the residue was distilled. We obtained 9.3 g (83% of theoretical) of n-butyl n-octylthioborate with b.p. 134-136° (0.05 mm); d_4^{20} 0.8770; n_D^{20} 1.4820. Found: C 63.75; 63.46; H 11.74; 11.80; B 3.40; 3.20%. $C_{16}H_{35}BS_2$. Calculated C 63.55; H 11.67; B 3.58%.

n-Butyl 2-phenylethylthioborate. A mixture of 6.8 g (0.018 mole) of tetra-n-butylmercaptodiborane, 4.0 g (0.038 mole) of styrene, and 0.5 ml of pyridine was heated for 3 hr at 70°. Subsequent fractionation yielded 3.1 g (30%) of n-butyl 2-phenylethylthioborate with b.p. 145-146° (0.02 mm); d_4^{20} 0.9827; n_D^{20} 1.5419. Found: C 65.06; 65.34; H 9.12; 8.99; B 3.86; 3.96%. $C_{16}H_{27}BS_2$. Calculated: C 65.29; H 9.29; B 3.67%.

n-Butyl cyclohexylthioborate. Similarly, from 7.4 g (0.019 mole) of tetra-n-butylmercaptodiborane, 3.2 g (0.039 mole) of cyclohexene, and 0.5 ml of pyridine we obtained 8.3 g of n-butyl cyclohexylthioborate (79% of theoretical) with b.p. 180-185° (4 mm). After redistillation, the ester had b.p. 155-156° (1 mm); d_4^{20} 0.9516; n_D^{20} 1.5737. Found: C 62.40; 62.26; H 10.87; 10.71; B 4.33; 4.38%. $C_{14}H_{29}BS_2$. Calculated: C 61.76; H 10.74; B 3.97%.

n-Butyl 2-methyldiethylsilylethylthioborate. 6.4 g (0.017 mole) of tetra-n-butylmercaptodiborane was mixed with a solution of 2-methyldiethylvinylsilane (5.3 g, 0.041 mole) in ether (10 ml) and 0.3 ml of pyridine and the mixture heated to boiling (50-55° in the reaction flask). Two fractionations yielded 3.7 g (37%) of n-butyl 2-methyldiethylsilylethylthioborate with b.p. 150-160° (0.5 mm). After redistillation, the ester had b.p. 156-158° (1 mm); n_D^{20} 1.5013; d_4^{20} 0.9224. Found: C 56.27; 55.96; H 11.16; 10.52; B 3.44; 3.48%. $C_{15}H_{35}BS_2Si$. Calculated: C 56.60; H 11.09; B 3.40%.

Action of propene on tetra-n-butylmercaptodiborane. 5 g (0.11 mole) of propene condensed at -40° was added to a cooled mixture of 7 g (0.018 mole) of tetra-n-butylmercaptodiborane and 0.3 ml of pyridine in a small autoclave. The reaction mixture was heated for 2 hr at 85° under a pressure of 15 atm. Three fractionations yielded: 1) 1.1 g (16.7%) of n-butyl di-n-propylthioborate with b.p. 97-105° (9 mm); n_D^{20} 1.4545 [literature data [2]: b.p. 98° (11 mm) n_D^{20} 1.4598]; 2) 1.5 g (17.8%) of n-butyl n-propylthioborate with b.p. 147-155° (9 mm) n_D^{20} 1.4919 [literature data [3]: b.p. 149-150° (13 mm); n_D^{20} 1.4956]; 3) 2 g (20%) of tri-n-butyl thioborate with b.p. 160-164° (2 mm); n_D^{20} 1.5205 (literature data [1]: b.p. 150° (1 mm); n_D^{20} 1.5265).

Action of isobutene on tetra-n-butylmercaptodiborane. Into a small autoclave were placed 8 g (0.021 mole) of tetra-n-butylmercaptodiborane and 0.3 ml of pyridine and then to the cooled mixture was added 10 g (0.17 mole) of isobutene, condensed at -30°. The reaction mixture was heated for 2 hr at 85° and a pressure of 5 atm. Three fractionations of the liquid reaction products yielded: 1) 2.3 g (25.6%) of n-butyl diisobutylthioborate with b.p. 112-113° (8 mm); n_D^{20} 1.4550 [literature data [2]; b.p. 107° (9.5 mm); n_D^{20} 1.4572]; 2) 2.8 g (27.4% of n-butyl isobutylthioborate with b.p. 141-142° (3.5 mm); d_4^{20} 0.9020; n_D^{20} 1.4919. Found: C 58.79; 58.79; H 10.96; 11.19%. $C_{12}H_{27}BS_2$. Calculated: C 58.51, H 10.85%; 3) 2.4 g (20.6%) of tri-n-butyl thioborate with b.p. 170-175° (4.5 mm).

SUMMARY

Tetra-n-butylmercaptodiborane reacts with unsaturated compounds at 70-80° in the presence of pyridine to form esters of alkylthioboric acids.

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SEPARATION OF STEROID ESTROGENS BY MEANS OF CHROMATOGRAPHIC PLATES

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The principle of chromatographic separation on an adsorbing surface, held appropriately on a glass plate, apparently was proposed for the first time by Izmailov and Shraiber in 1938 [1]. This procedure was subsequently developed considerably. In 1949 Meinhard and Hall [2] successfully used it for the radial separation of metal ions. Kirchner, Miller, and Keller [3] in 1951, Reitsema [4] in 1954, and Stahl [5] in 1956 helped with the further development of this chromatographic method. In 1956, Demole applied the method of separation by chromatographic plates to many classes of compounds: terpene alcohols, phenols, essential oils, etc. [6-8]. In 1959, Barbier described the separation of natural p-benzoquinones by this method [9]. Barbier, Jager, Tobias, and and Wyss [10] were able to separate some steroid derivatives, mainly aetianic esters.

In the present communication, we describe the behavior of estrogenic hormones on chromatographic plates. In our opinion, the simplicity, speed, and sensitivity of this method make it preferable to paper chromatography as a stationary phase must be used in the latter case [11] (propylene glycol, formamide, or silicone oil). A chromatographic analysis on a plate may be carried out in 30 min. Under the conditions we describe, there was high sensitivity with 10-25-γ samples; in the case of estrone, it was possible to detect a 0.5-γ sample. This method is particularly valuable for studying fractions obtained by chromatography on a column. It makes it possible to obtain information immediately on the separation during the course of the actual operation and check the purity of the fractions. The given method may also be a practical means of investigating estrogens in biological media. Our experiments were carried out on 8 samples of estrogen hormones: estrone, estrone acetate, the methyl ether of estrone, estradiol, the 3-methyl ether of 17-ethynyl-estradiol, equilin, isoequilin, and lumiestrone.

EXPERIMENTAL

We used Pyrex glass plates (17 × 11 cm), covered with a mixture of silicic acid (Mallinckrodt or Merck reagent), gypsum (5%), and water (approximately 3 times the mixture by volume). The plates were left for 30 min with the surface exactly horizontal and then activated by heating for 1 hr in a drying cupboard at 110°. The same operations were carried out as in paper chromatography and the plates were placed in a vessel containing a system of solvents (ascending chromatography). The gypsum may be replaced by starch (5%), which gives a stronger adsorbing layer, but then it is not possible to use antimony trichloride (25% solution in chloroform, heating at 200-250°) as a developer. When starch is used as the fixer, development may be carried out with iodine vapor or immersion for 5 sec in 0.5% potassium permanganate solution with subsequent washing with water; the R_f values were close to those obtained when gypsum was the fixer, but the development sensitivity was lower and the edge of the spots was less sharp.

Examples of Separation

Example 1 (Fig. 1)

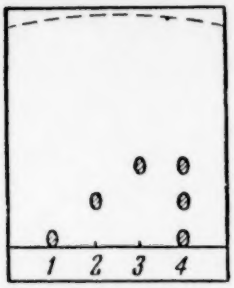

Fig. 1. Estrone, 25 γ, R_f 0.05 ± 0.05; 2) estrone acetate, 25 γ, R_f 0.17 ± 0.05; 3) methyl ether of estrone, 25 γ, R_f 0.35 ± 0.05. Solvent system: pentane–ethyl acetate, 9:1. Developer: $SbCl_3$ in chloroform; heating at 200-250°; examination in ultraviolet light.

Example 2 (Fig. 2)

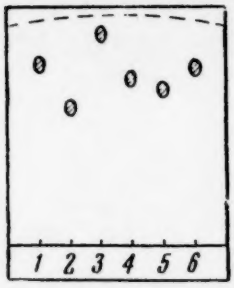

Fig. 2. Estrone, 25 γ, R_f 0.72 ± ±0.05; 2) estradiol, 25 γ, R_f 0.40 ± 0.05; 3) methyl ether of ethynylestradiol, 25 γ, R_f 0.83 ± ± 0.05; 4) equilin, 25 γ, R_f 0.66 ± ± 0.05; 5) isoequilin, 25 γ, R_f 0.6 ± 0.05; 6) lumiestrone, 25 γ, R_f 0.70 ± 0.05. Solvent system: pentane–ethyl acetate 3:2. Developer: see above.

Example 3 (Fig. 3)

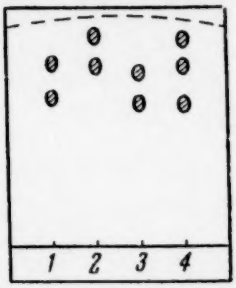

Fig. 3. Estrone + estradiol; 2) estrone + methyl ether of ethynylestradiol; 3) estradiol + + equilin; 4) estrone + estradiol + methyl ether of ethynylestradiol. Solvent system: pentane–ethyl acetate 3:2. Developer: see above.

It was not possible to separate mixtures of estrone and lumisterol or equilin and isoequilin under the conditions described above.

In conclusion, we would like to thank E. Lederer for the interest he showed in this work and also A. Horeau and J. Jacques for providing steroid samples.

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LETTERS TO THE EDITOR

ADSORPTION OF METHANOL ON POTASSIUM SULFATE LABELED WITH ^{35}S

V.I. Spitsyn, I.E. Mikhailenko, A.V. Kiselev, and L.D. Belyakova

Institute of Physical Chemistry, Academy of Sciences, USSR
Translated from Izvestiya Akademii Nauk SSSR,
Otdelenie Khimicheskikh Nauk, No. 7, p. 1311, July, 1960
Original article submitted February 26, 1960

Sir:

Radioactive radiation of solids affects their physicochemical properties [1, 2]. In particular, the adsorption of various organic dyes from an aqueous medium on $BaSO_4$ depends on the α- or β-emitters present in it. The emission of charged particles evidently produces additional electrical charges and gradually increases the number of active centers on the surface. Inactive (1) and ^{35}S-labeled preparations of K_2SO_4 (2 and 3) were used. To part of a solution of inactive K_2SO_4 was added a solution of radioactive Na_2SO_4 with ^{35}S. The solutions were evaporated, the salts fired at 700-800°, and fractions collected at 0.17-0.10 mm. The activity was measured on an end-window counter. The activity of preparation 2 immediately after preparation was 21.9 and before the experiments (after 30 days), 17.2 mC/g, while for preparation 3, the activities were 2.3 and after 473 days, 0.08 mC/g, respectively. The adsorption of methanol vapor after the samples had been pumped out at 200° was measured on the apparatus described in [3]. In comparison with the adsorption on preparation 1, the adsorption on active preparations 2 and 3 was increased by 20 and 40% respectively (at a relative vapor pressure of 0.2). Thus, the introduction of ^{35}S into the sample increased the adsorption of methanol, and not only the activity in the freshly prepared sample was important, but also the time for which it had been kept.

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ISOTOPIC EXCHANGE BETWEEN DIALKYLMERCURY AND ALKYLMERCURIC BROMIDE

O.A. Reutov, T.P. Karpov, É.V. Uglova, and V.A. Malyanov

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Translated from Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk, No. 7, pp. 1311-1312, July, 1960
Original article submitted April 7, 1960

Sir:

In developing previous work on isotopic exchange of organomercury compounds [1-3], we found a new type of reaction of alkylmercury compounds:

$$RHg^{203}Br + R_2Hg \rightleftarrows RHgBr + R_2Hg^{203},$$

where

$$R = -CH(CH_3)CH_2CH_2CH(CH_3)_2$$

The isotopic exchange was carried out in absolute alcohol at 60° in the dark. The mixture was separated chromatographically on Al_2O_3. With the concentrations of the starting materials both equal to 0.05 M, the half-exchange period was ~4 hr. To study the mechanism of the reaction, we used an optically active alkylmercuric bromide with $R = -CH(CH_3)CH_2CH_2CH(CH_3)_2$, which was obtained previously [4]. The isotopic exchange was accompanied by a gradual distribution of the optical activity between the dialkylmercury and the alkylmercuric bromide. The rates of the isotopic exchange of mercury atoms and the distribution of radicals were equal. The configuration of the asymmetric carbon atom attached to the mercury was retained during the reaction. The results obtained indicate that the isotopic exchange examined is the result of the following reversible processes (R is the optically active radical):

$$\dot{R}Hg^{202}|X + R|HgR \rightleftarrows \dot{R}|Hg^{204}R + X|HgR \rightleftarrows RHg|\dot{R} + X|Hg^{203}R$$

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*Original Russian pagination. See C.B. translation.

CATALYTIC HYDROGENATION OF LIGNIN

N.A. Vasyunina, A.A. Balandin, S.V. Chepigo, and G.S. Barysheva

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Translated from Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk, No. 7, p. 1312, July, 1960
Original article submitted April 29, 1959

Sir:

Despite the vast resources of lignin, it is not yet used sufficiently chemically; its structure has not been established conclusively. New reactions of this substance are therefore of great importance. A number of authors have hydrogenated lignin catalytically over Ni, $CuCr_2O_4$, etc.; lignin is thereupon converted into hydrocarbons to a considerable extent. In contrast to this, we were able to develop a hydrogenation method whereby lignin is wholely converted into water-soluble compounds. The catalyst was Ru, which we used previously to develop the hydrolytic hydrogenation of cellulose [1].

We present the results of a typical experiment: 10 g of hydrolyzed pine lignin in 200 ml of 2% aqueous NaOH with 0.5% Ru (on charcoal, 0.5%) was heated for 2.5-3 hr at 300-320° under 200 atm of hydrogen. The catalyzate was a colorless or pale-yellow solution with a strong phenolic smell and was filtered to remove catalyst and acidified; no lignin precipitated. There was no hydrocarbon layer. After the catalyst had been washed with hot water, it could be reused for the reaction.

Paper chromatography showed that the aqueous solution contained phenol, m-cresol, and pyrocatechol. The yield of the mixture of phenols was 30-40%. The result obtained agrees with the opinions of Freudenberg that the structural units of lignin are derivatives of coniferyl alcohol.

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CHRONICLE

GENERAL MEETING OF THE DIVISION OF CHEMICAL SCIENCES OF THE ACADEMY OF SCIENCES OF THE USSR ON MARCH 24,1960

Translated from Izvestiya Akademii Nauk SSSR,
Otdelenie Khimicheskikh Nauk, No. 7, pp. 1313-1315, July, 1960

A General Meeting of the Division of Chemical Sciences of the Academy of Sciences of the USSR, devoted to reports on the chemistry of plant materials, was held on March 24, 1960, under the chairmanship of A.P. Vinogradov. Corresponding Member Acad. of Sci., USSR,N.I. Nikitin,reported on the chemical composition and use of larch wood and its gum (arabogalactan). The author reported that the area covered by larch in Siberia and the Far East is twice as great as that occupied by spruce and pine together in the whole of the Soviet Union. The use of larch in the cellulose industry began only very recently; the water-soluble polysaccharide of larch, arabogalactan, is not used at all, when the wood of daurskii larch, for example, contains an average of 10-12% of it (daurskii larch probably refers to Larix dahurica).

Many laboratory experiments on the preparation of sulfate cellulose from wood of daurskii larch showed the advantage of a preliminary separation of arabogalactan and other water-soluble substances from it with water by heating in an autoclave. The removal of water-soluble substances in cellulose factories before the wood is boiled with technical solutions of sodium hydroxide containing various amounts of sodium sulfide makes it possible to reduce the consumption of active alkali by 4-5% in the preparation of cellulose with a comparable degree of delignification. As regards chemical properties, cellulose samples prepared were pure and showed, in part, molecular heterogeneity. It was shown that larch wood may be used to prepare soft viscose cellulose with a high content of the stable α-fraction (up to 96%), a low ash content, and with good viscosity and filtration characteristics of the xanthate solutions. It was shown that arabogalactan and other water-soluble substances of larch may be used for the preparation of alcohol by hydrolysis. These substances are hydrolyzed quantitatively by 0.15% sulfuric acid at 160° after 10-15 min. When the substances extracted with water were fermented with a culture of Schizosaccharomyces yeast, 1 ton of larch wood could yield an additional 90-100 liters of ethanol if the wood were converted to sulfate cellulose and the substances preliminarily extracted with water, to alcohol. On the basis of the investigations, a scheme was recommended for processing larch wood. As the author reported, experiments on the preparation of dulcitol by hydrogenation of hydrolyzed arabogalactan, which were carried out in the Institute of High Molecular Compounds, Academy of Sciences USSR in cooperation with the Leningrad Institute of Petroleum Processing, showed that in the presence of a stationary industrial nickel hydrogenation catalyst on a kieselguhr base at a hydrogenation temperature of 120° and a pressure of 150 atm, the yield of crude dulcitol after the first 36 hr of continuous catalyst operation was 97% of the starting reagents.

The preparation of sulfite cellulose requires special methods for the preliminary removal of arabogalactan (treatment with very dilute solutions of sodium hydroxide at 50-60°) to avoid condensation of lignin which hampers its removal from wood chips. The author reported that in connection with the construction of large new plants in Siberia, the Paper Institute, the Hydrolysis Institute, and Planning Organizations are now carrying out a large amount of work both on the preparation of cellulose from larch and on the hydrolysis of its gum.

Academician of the Academy of Sciences of the Latvian SSR A.I. Kalninsh gave a report on new possibilities on the use of plant wastes. He noted the importance of the resolutions of a series of reports on wood chemistry at a session of the division of Chemical Sciences and described work on the swelling of cell walls of spruce wood, carried out in the Institute of Silviculture Problems and Wood Chemistry of the Academy of Sciences of the Latvian SSR. It was established that lignin of the cell walls swells to the same extent as cellulose.

Hemicelluloses swell four times as much. It was shown that sugars and also preliminary thermal treatment have an effect on the swelling of wood. On the basis of the investigations of the physicochemical properties of cell walls and their components, two variants were developed for the hydrolysis of plant wastes (pine wood) by concentrated sulfuric acid, which give a sugar yield up to 67% with solution concentrations of 10-18%. In the first variant 1-1.5 parts of sulfuric acid was used to 1 part of vegetable material with subsequent use of acid for the production of a food or fertilizer precipitate. In the second variant, the hydrolysis required 0.1-0.3 parts of acid to 1 part of vegetable material.

The author reported that existing methods of preparing cellulose involved the formation of vast amounts of harmful wastes, which contaminate reservoirs and the atmosphere and therefore new methods should be developed. Among these is the hydrotropic method of preparing cellulose and hemicellulose, which was developed in the Institute of Silviculture and Wood Chemistry of the Academy of Sciences of the Latvian SSR. Cellulose of satisfactory quality may be obtained from larch wood by this method. Together with cellulose, the method yields active lignin which is suitable for the replacement of phenol in phenol-formaldehyde plastics, and also in the production of strong lignin-fiber tiles.

The author reported that the Institute has developed a method of using brushwood, branches and other fine lumber wastes in the form of compressed blocks suitable for use in construction and as a chemical raw material. A number of methods of processing vegetable wastes proposed by the Academy of Sciences of the Latvian SSSR have been adopted in the plants of Latvia and other Soviet Republics.

Doctor of Chemical Sciences N.N. Shorygina (coauthors: A.A. Chuksanova, L.L. Sergeeva, T.V. Izumrudova, N.P. Mikhailov, and V.D. Tychina) gave a report on the nitration of lignin and model compounds and the use of nitrolignin in industry. The author noted the lack of knowledge of the chemistry of ligneous substances, for which reason, these polymers, which form 30% of the weight of wood and, after cellulose, are the most widespread natural organic substances on earth, have remained until now large-scale, useless wastes from wood processing. One of the reactions of lignin which has been studied little is nitration. This reaction, which leads to a modification of the properties of lignin, is of interest both from the point of view of possible uses of lignin in the national economy and from the point of view of obtaining some data on the structure of lignin. Ligneous substances, which are polycondensation products of substituted phenols, are readily nitrated by dilute nitric acid.

Depending on the nitration conditions and the origin of the starting material, the nitrolignins obtained differ considerably with respect to the content of functional groups, solubility, and other properties. Their nitrogen content is more or less constant (~4% in coniferous species). Together with nitration, treatment with nitric acid results in oxidation of lignin and its partial destruction and also, apparently, a number of other secondary reactions. In order to determine the behavior of separate fragments of a lignin molecule during nitration, the nitration of model compounds, which may be regarded as structural elements or fragments of lignin, was studied. As models, we chose guaiacylveratrylpropanols with the alcohol hydroxyl groups in various positions in the chain and also the α-guaiacyl ether of β-veratrylglycerol and guaiacylacetone. The models were chosen as lignin contains similar structures. The nitration was carried out with fuming nitric acid in carbon tetrachloride at 5°. Results were obtained which make it possible to explain some of the peculiarities of lignin during nitration. Lignin is also nitrated readily by dilute nitric acid (5-10%) in the presence of nitrite even at 40-50°. The nitrolignins obtained contain 3% of nitrogen and 8-10% of carboxyl groups and are readily soluble in dilute solutions of alkalis and some organic solvents; they were good reducers of viscosity and shear stress of clay mortar used in drilling oil and gas wells and have been used successfully for this purpose in well drilling in the Soviet Union.

Engineer M.A. Ivanov (coauthor Prof. D.V. Tishchenko) gave a report on a new method of preparing high-percentage α-cellulose. The author stated that in recent years it has been found that the spinning of viscose with drawing in the presence of precipitation retarders makes it possible to obtain extremely strong fiber. The strength of the fiber is directly proportional to the α-cellulose content of the starting material. The production of fiber with a breaking length of more than 50 km requires cellulose containing not less than 96% of α-cellulose. Such cellulose may be obtained by enriching normal technical cellulose, containing 86-88% of α-cellulose, but this involves large chemical loss of cellulose with high consumption of reagents, labor, and subsidiary facilities. This has produced searches for methods of preparing high-percentage α-cellulose directly from wood.

For the preparation of cellulose it is necessary to dissolve hemicelluloses, pentosans and lignin. Hemicelluloses and pentosans are readily dissolved by heating with dilute acids, but lignin condenses under these

conditions and becomes difficultly soluble with any method of boiling the wood. The chemical nature of the "condensation and inactivation" of lignin has remained unknown up to now. The authors put forward a hypothesis which considers and explains a very large amount of experimental data from one point of view; this was based on the analogy in the chemical structure of lignin and phenolic alcohols. It was shown that the introduction of sulfonyl groups into phenol, phenolic alcohols, or novolak sharply reduces their polycondensation rate. Hence it follows that even slight preliminary sulfonation of lignin under mild conditions with sulfite–sulfurous acid should protect it from condensation with a subsequent increase in the acidity of the medium, necessary for dissolving the hemicelluloses and pentosans. The investigators showed that preliminary sulfonation of lignin protects it from condensation in a strongly acid medium, the danger of a "black boil" is eliminated, and it became possible to use the phenomenon of a "black boil" (an increase in acidity) for dissolving hemicelluloses and pentosans. On the basis of the considerations presented and the experimental data, M.I. Ivanov developed and checked on laboratory and pilot-plant scales a new industrial process for preparing high-percent α-cellulose directly from wood: The boiling solution of the first stage was prepared by saturating green alkali from sulfate cellulose production (Na_2CO_3+ Na_2S) with sulfur dioxide to a concentration of 4-6% total and ~1-1.5 % bound SO_2, when a certain amount of thiosulfate and elementary sulfur was formed in the solution. The chips were kept in this solution for not more than 5 hr at a temperature of no higher than 105°; preliminary sulfonation of the lignin was thus achieved. The temperature was then raised to 120° and in the presence of thiosulfate and sulfur there was an oxidation–reduction reaction so that the sulfurous acid was converted to sulfuric acid, leading to hydrolysis of the hemicelluloses and pentosans. The boiling solution was then drained away and replaced by white alkali from sulfate cellulose production (NaOH+ NaSH) and the cellulose boiled at 170°. The lignin then dissolved in the form of the sodium salts of lignosulfonic acids and as alkali lignin. The combined alkalis from the first and second stages of the boil were regenerated by the normal sulfate scheme. The cellulose obtained contained ~ 97% of α-cellulose and had a very high reactivity.

Academician A.A. Balandin (coauthors N.A. Vasyutina and S.V. Chepigo) reported the preparation of polyhydric alcohols and phenols by catalytic processing of plant materials. The author reported the development of processes which offer great possibilities for the efficient use of the plant wealth of the country. Thus, hydrolytic hydrogenation of cellulose and hemicellulose in an acid medium (0.7% phosphoric acid) in the presence of a ruthenium catalyst (0.3%) made it possible to obtain sorbitol in 95% yield. Hydrogenation of sorbitol in a neutral medium with a nickel catalyst yielded glycerol (in up to 35% yield) and propylene glycol (35%). Analogously, xylitol yielded glycerol and ethylene glycol. Hydrogenolysis of lignin with a ruthenium catalyst in an alkaline medium yielded phenol, m-cresol, and pyrocatechol in 30-40% yield. The author noted that polyhydric alcohols and phenols are of importance in the production of artificial fibers, synthetic resins and plastics, and also surface-active substances.

Prof. P.N. Odintsov, A.F. Zaitseva, Prof. V.I. Sharkov, Academician of the Acad. Sci. Kirg. SSR V.I. Ivanov, and Corresponding Member Acad. Sci. USSR S.N. Danilov participated in the discussion of the reports.

In summarizing the reports, Academician A.P. Vinogradov noted the importance of the work presented in the national economy and pointed out the need for closer cooperation between chemists of the Institutes of the Academy of Sciences USSR and the technologists of branch institutes and industry.

Academician A.P. Vinogradov stated that the time is ripe for the transfer of the direction of the hydrolysis industry and the refinement of techniques in hydrolysis processes from the forestry and wood processing industry to the State Committee of the Council of Ministers of the USSR for chemistry. The corresponding scientific research and planning organizations obviously should be transferred to the same committee.

SIGNIFICANCE OF ABBREVIATIONS MOST FREQUENTLY ENCOUNTERED IN SOVIET PERIODICALS

FIAN	Phys. Inst. Acad. Sci. USSR.
GDI	Water Power Inst.
GITI	State Sci.-Tech. Press
GITTL	State Tech. and Theor. Lit. Press
GONTI	State United Sci.-Tech. Press
Gosenergoizdat	State Power Press
Goskhimizdat	State Chem. Press
GOST	All-Union State Standard
GTTI	State Tech. and Theor. Lit. Press
IL	Foreign Lit. Press
ISN (Izd. Sov. Nauk)	Soviet Science Press
Izd. AN SSSR	Acad. Sci. USSR Press
Izd. MGU	Moscow State Univ. Press
LEIIZhT	Leningrad Power Inst. of Railroad Engineering
LET	Leningrad Elec. Engr. School
LETI	Leningrad Electrotechnical Inst.
LETIIZhT	Leningrad Electrical Engineering Research Inst. of Railroad Engr.
Mashgiz	State Sci.-Tech. Press for Machine Construction Lit.
MEP	Ministry of Electrical Industry
MES	Ministry of Electrical Power Plants
MESEP	Ministry of Electrical Power Plants and the Electrical Industry
MGU	Moscow State Univ.
MKhTI	Moscow Inst. Chem. Tech.
MOPI	Moscow Regional Pedagogical Inst.
MSP	Ministry of Industrial Construction
NII ZVUKSZAPIOI	Scientific Research Inst. of Sound Recording
NIKFI	Sci. Inst. of Modern Motion Picture Photography
ONTI	United Sci.-Tech. Press
OTI	Division of Technical Information
OTN	Div. Tech. Sci.
Stroiizdat	Construction Press
TOE	Association of Power Engineers
TsKTI	Central Research Inst. for Boilers and Turbines
TsNIEL	Central Scientific Research Elec. Engr. Lab.
TsNIEL-MES	Central Scientific Research Elec. Engr. Lab.–Ministry of Electric Power Plants
TsVTI	Central Office of Economic Information
UF	Ural Branch
VIESKh	All-Union Inst. of Rural Elec. Power Stations
VNIIM	All-Union Scientific Research Inst. of Metrology
VNIIZhDT	All-Union Scientific Research Inst. of Railroad Engineering
VTI	All-Union Thermotech. Inst.
VZEI	All-Union Power Correspondence Inst.

Note: Abbreviations not on this list and not explained in the translation have been transliterated, no further information about their significance being available to us. – Publisher.

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Indole-3-Acetic Acid (Heterouxin)
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5-Methylisatin
2-Methylindole-3-Propionic Acid
2-Isoindolineethanol

SYNTHESES OF HETEROCYCLIC COMPOUNDS

Edited by
A. L. MNDZHOIAN

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5-(Diethylaminomethyl) Furfuryl Alcohol
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Methyl 5-(Bromomethyl)-2-Furoate
Methyl 5-(Diethylaminomethyl)-2-Furoate
Methyl 5-Methyl-2-Furoate
Methyl 5-(Propoxymethyl)-2-Furoate
Methyl 2-Furoate
Methyl 5-(Chloromethyl)-2-Furoate
2-Methylfuran (Sylvan)
5-Methyl-2-Furoic Acid
5-(Propoxymethyl)-2-Furoic Acid
Furan

5-(Aminomethyl)-2-Furoic Acid
5-Benzylfurfuryl Acetate
2-Furyl Methyl Ketone
2-Benzylfuran
5-Benzylfurfuryl Alcohol
5,5'-(Thiodimethylene) Di-2-Furoic Acid
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Diethyl Furfurylidenemalonate
5-Carboxy-2-Furanpropionic Acid
Methyl Tetrahydro-5-Methyl-2-Furoate
Methyl 4-(Chloromethyl)-5-Methyl-2-Furoate
Methyl 5-(Cyanomethyl)-2-Furoate
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